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FURTHER NOTES ON THE GROWING OF WHEAT IN ONE-SALT SOLUTIONS

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By employing certain combinations of one-salt nutrient solutions and systematically changing the cultures growing therein from one solution to another, the writer (1) has shown that wheat seedlings grow about as well, for at least one month[1] with only two nutrient elements (one salt) present in the media at a time, as they do in complete, well-balanced, nutrient solutions. It was held that these results showed that the proper pairing of certain of the nutrient cations with anions operated as a very important physiological condition in the growth media of the plants. The term "proper pairing" of the ions is not meant to convey the idea that the intake of nutrient mineral elements by the plant was conditioned by the law of definite chemical proportions, either for the absorption of two ions of opposite charge or any other group of atoms. But the conclusion drawn from the results of the experiment was that there are elements whose availability to and utilization by the plants is dependent upon certain other elements in the medium. These ions being of opposite charge are, therefore, considered as being physiologically paired. This proper pairing of the ions, therefore, would designate a salt which, when used singly, would give greater growth of plant than any other nutrient salt used singly that contains but one of these so-called properly paired elements. If these conclusions are stated in a concrete way, they are as follows:

The absorption and utilization of nitrates by the wheat plant is largely dependent upon the relative supply of available potassium in the medium. If either potassium or nitrate is to be utilized, both must be present and absorbed at the same time. The utilization of these elements by the plants, on the other hand, is largely independent of the presence at the same time, of other essential ions, namely, Ca, Mg, PO_4 and SO_4, and perhaps Fe, though the effect of the absence of this latter element has not been experimentally determined. That

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[1] Judging from an experiment now in progress, it appears to be possible to grow wheat plants to maturity by the method referred to in the paper cited, that are equally as good as those grown in any of the complete, well-balanced, nutrient solutions tested by the writer. Plants now ten weeks old growing in solutions of KNO_3, $CaSO_4$ and $MgHPO_4$, and changed systematically from one solution to another, are fully as large as those growing simultaneously in the control complete nutrient solutions. The set of cultures giving best growth to date is one where the plants are in a solution of KNO_3, 4 days; $CaSO_4$, 1 day; and $MgHPO_4$ 1 day. These different solutions are each of 0.01 mol. concentration.

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is, these other elements are not needed to make potassium or nitrate physiologically available. Obviously, all essential elements must be accessible to the plant at times and at frequent enough intervals. They are important and needed for the growth of the plants, and this growth of the plant, undoubtedly, is in itself, a very important factor that affects not only the absorption and utilization of potassium and nitrate, but also that of all other needed elements.

Following up the investigation already referred to, which bore on the physiological importance of the relations between certain of the essential elements, data obtained from some recent simple experiments appear to throw further light on this important condition affecting the growth of wheat plants.

Cultures of wheat seedlings were set out in 1-quart jars filled with tap water which had a total salt concentration equal approximately to 0.1 atmosphere osmotic pressure. The elements that constituted the principal salts of the tap water were Ca, Mg, Na, SO_4, Cl. The plants remained in this medium for four months. The water was not renewed, save to replenish that lost by transpiration of the plants. During the first two months in tap water, the plants made some shoot growth attaining to a height of 14–20 cm. During this time, the plants made a very large root growth (2). The root mass attained at the end of this period varied from 90 to 120 cm. in length for different cultures. Approximately 50 per cent of the dry weight of the plants was contained in the roots. During the last two months that the cultures were in tap water, there was no apparent evidence of new growth of tops. As to the roots, it may be stated that growth appeared to have ceased three or four weeks before the end of the four months period. These plants of pale green and starved appearance which made no aerial growth for at least two months, but nevertheless possessed the ability to renew growth if placed in a good complete nutrient solution, were then transferred to the single salt solutions to be tested. One-quart containers were used and ten cultures were used for each test of the different salts. There was no further change of solution during the test of the remaining growth period of the plants, except the replenishment of water lost by transpiration. A trace of iron ($\frac{1}{2}$ cc. of 0.01 mol. $FeSO_4$) was added at intervals to the cultures. Some of the results obtained are given in table 1.

Ten days after the cultures had been transferred to the different salt solutions, it was noted that the plants placed in solutions containing nitrogen were greener than those placed in solutions that did not contain nitrogen. Within two to three weeks, new growth in the form of tillers began to appear at the base of plants placed in the solutions of KNO_3, the solutions of $Mg(NO_3)_2$ and in the complete nutrient solutions, the latter being employed as controls. The tillers that started on the plants growing in KNO_3 solution and the complete nutrient solution appeared to be normal. They grew and gained in height. But the tillers that started on the plants placed in $Mg(NO_3)_2$ grew only to a height of 1–2 cm., then, due to abscission of the tips of the leaves and shoots, which is a characteristic phenomenon of cereal seedlings growing in certain unbalanced solutions, they could not elongate. A whorl of small,

deformed leaves, some of which died before the plants had lost their green color, was all the evidence of new growth obtained due to $Mg(NO_3)_2$. The plants of this set were the first ones to die. There was no evidence of new growth of the aerial portions of the plants placed in any of the solutions that did not contain nitrates. On the other hand, new roots started on the plants placed in the following solutions, KNO_3, $CaSO_4$, $CaHPO_4$ and $Ca(H_2PO_4)_2$, $MgHPO_4$ and $Mg(NO_3)_2$. The new roots that formed on the plants placed in $Mg(NO_3)_2$ soon died.

TABLE 1

*Some effects of single salt nutrient solutions on the renewal of growth of wheat seedlings**

SALTS USED	CONCENTRA-TION OF SOLUTION	GROWTH RESPONSES	
		Tops	Roots
	mol.		
KH_2PO_4	0.010	No new growth	Little growth
KNO_3	0.010	Greening of leaves, formation of tillers, elongation of original stalks and tillers	New growth arising from root crown
K_2SO_4	0.010	No new growth	No apparent growth
{ $CaHPO_4$	Saturated		
{ CaH_2PO_4	0.001	No new growth	Some new growth
$Ca(NO_3)_2$	0.010	Greening of leaves, no new tillers	Some new growth
$CaSO_4$	0.010	No new growth	Little growth
$MgHPO_4$	0.010	No new growth	Very small amount of new growth
$Mg(NO_3)_2$	0.010	Greening of leaves, formation of new tillers which did not grow more than 2 cm. because of abcission caused by salt—plants were the first of experiment to die	A few new roots appeared but they soon died
$MgSO_4$	0.010	No new growth	No apparent growth
{ KH_2PO_4 † { $Ca(NO_3)_2$ { $MgSO_4$	0.010	Greening of leaves and much new growth of tillers and stalks	Much new growth

* By renewal of growth is meant greening of the leaves and formation of new leaves or tillers.

† This was a complete nutrient solution composed of equal concentration of the three salts.

Of the nine different single salt-solutions used as growth media for wheat seedlings, only those plants in the solution of KNO_3 produced appreciable growth. It was not as large as that produced by the plants placed in the complete nutrient solution, but, nevertheless resulted in significant increase of dry matter. As the tap water of the laboratory in which these plants were kept for four months contained appreciable amounts of Ca, Mg and SO_4, it appears that the plants may have absorbed certain amounts of these elements which possibly could have been used in a later growth phase. Potassium and

nitrogen were notably deficient in the tap water. It was only when these two elements were later contained in the growth medium of the plants that fairly good growth was obtained from wheat seedlings which had ceased growing for two months.

It is fully appreciated that wheat plants cannot grow in the absence of either potassium or nitrogen. That they did renew their growth in media where these two elements were present does not necessarily, by itself, imply a potassium-nitrogen relation as a physiological requirement for growth. But, in view of the findings of the experiment already referred to where it was only under those conditions where potassium and nitrogen were supplied together, other things being equal, that good growth was obtained and very poor growth when the two elements were not supplied together, the results here reported appear to be the only logical ones that could be expected to occur.

The reasons for this can be briefly stated:

(a) KNO_3 supplied the wheat plant with two essential elements that are obtained by the plant through its roots. Apparently these two are needed in a greater quantity than any of the other mineral elements.

(b) KNO_3 supplied the wheat plant with two elements that must be present at the same time in the growth medium in order that either of these essential elements can be utilized by the plants.

The results of these experiments with single salt solutions appear to have defined, at least in part, the basis that underlies the conditions for physiological balance between potassium and nitrogen in the culture solution of wheat plants. But the fact that KNO_3 is the salt of potassium and of nitrogen which can be used singly to produce as good growth of wheat as was produced in the solutions of the six different types of three salt combinations used (1), does not mean that in order to obtain the best growth of wheat in a complete nutrient solution that potassium and nitrate must be present in that solution in the ratio that these elements are found in KNO_3. Neither does it mean that KNO_3 is the best salt of potassium or of nitrogen to use to obtain the best growth of wheat plants in complete nutrient solutions. Experiments have shown that differences of ratios of ions in nutrient solutions may vary over a considerable range of values without any apparent correlatable differences in resulting growth of plant. This conclusion is further substantiated by the fact that the ratios of the essential mineral elements for plant growth as determined by the analysis of the water-soluble constituents of apparently equally productive soils cover a comparatively wide range of values. These facts, of course, in no way militate against the validity of the argument that the relations of the quantities of one element to that of another or others are physiologically important. It simply means that there appears to be no definite single ratio of a stated value of element to element that defines the one best set of conditions for the growth of plants in complex media. That there should be one best set of conditions for the growth of plants can hardly be expected in

the light of what is known of the effects of the interrelations of the factors (essential and non-essential) that influence plant growth. There appears to be a great array of different conditions under which plants do equally as well. This apparently must come as the result of the operation of Le Chatelier's law which appears to be equally applicable to biological processes as to chemical and physical, that is, that any alteration in the factors which determine an equilibrum causes the equilibrium to become displaced in such a way as to oppose, as far as possible, the effect of the alteration.

It appears that the physiological effect or the fertilizing efficiency of nitrogen is not primarily conditioned by the available supply of that element, but is affected in no small degree by the relation of the supply of that element to that of another, namely, potassium. The relation between these determines in no small measure whether one of the elements is deficient or not. Obviously the magnitude of available supply of any of the necessary elements in the growth media of plants is important because a certain minimum amount is required for normal metabolic processes of the plants, and because this factor (magnitude of supply) determines the relation of the actual mass of the one to that of any other.

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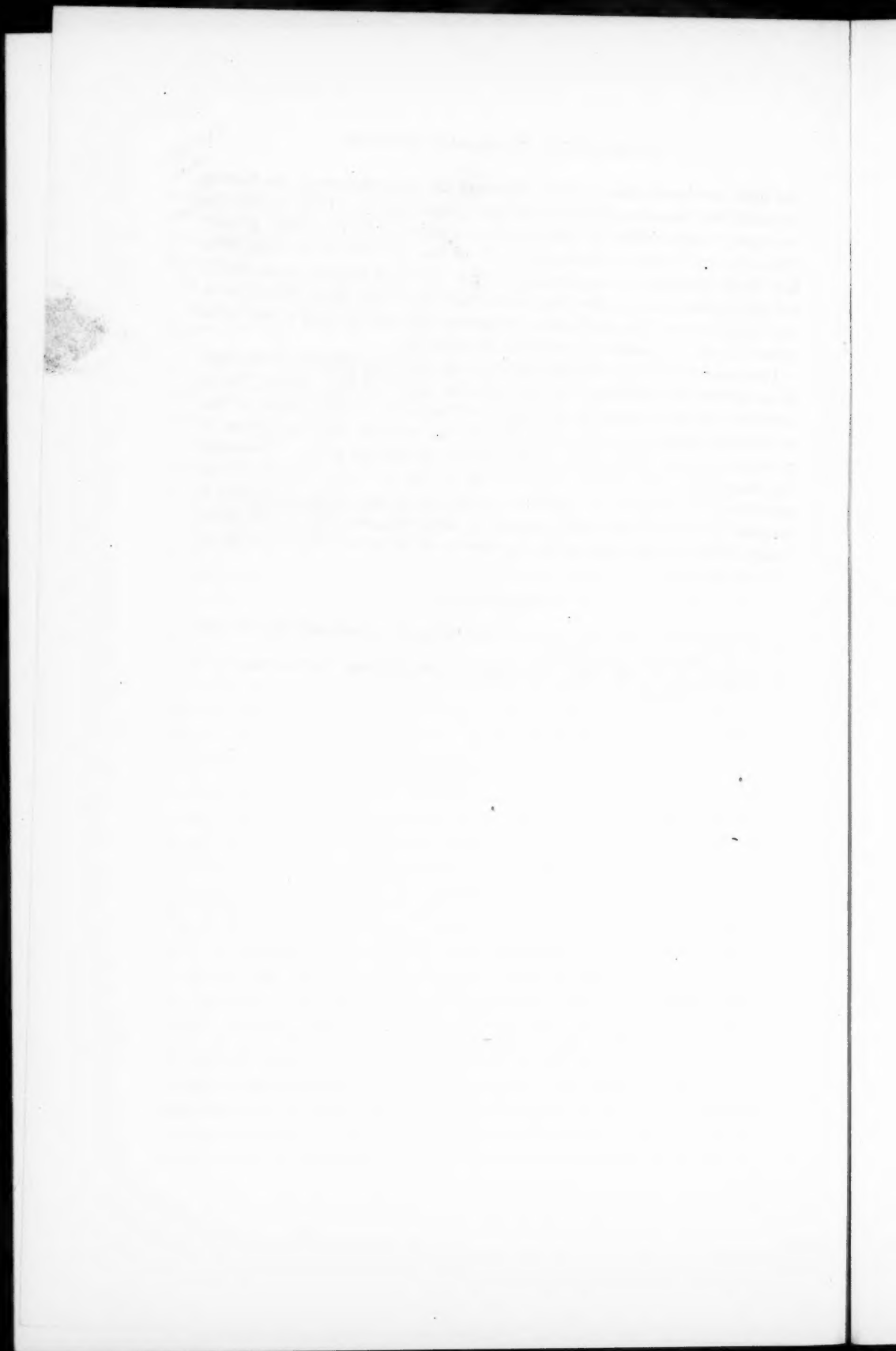
RELATIONS BETWEEN CALCIUM CARBONATE, CERTAIN FERTILIZER CHEMICALS AND THE SOIL SOLUTION[1]

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SOLUBILITY OF CALCIUM CARBONATE IN SOIL SOLUTION

The application by Johnston (9), of the fundamental laws of solutions to the relations between calcium carbonate in a solution and carbon dioxide in the atmosphere above it, has led the writer to study the relation of those laws to the use of lime in agriculture.

Lime is applied to the land in the forms of calcium carbonate, calcium hydrate or calcium oxide, depending on the economic conditions that surround its purchase and transportation. Its relatively low initial cost results in its application in large quantities per acre compared with most chemical fertilizers. It has been shown by MacIntyre (14) that the final stable form of lime in the soil is calcium carbonate, therefore the soil-solution under the conditions of customary applications of lime must be saturated with that compound for a considerable period.

Carbon dioxide is the important variable in the soil-solution because the range of its proportion in the soil-air is very wide in comparison with that in the free air above the soil. Air in the open country is remarkably uniform in its content of carbon dioxide; but in the soil, where the air must remain more or less stagnant, the respiration of the living organisms may cause the carbon dioxide to rise to high proportions as in ill ventilated rooms.

Carbon dioxide in the soil has received considerable attention by investigators and has been found to vary with soil and with crop. Russell (18) recapitulates such investigations and shows a range from 0.4 per cent to 2.3 per cent in pasture land, while as low as 0.05 per cent has been observed in bare sandy soil.

Turpin (24), in some vegetation experiments with pots, found a maximum of 3.34 per cent CO_2 in the air of a clay soil on which a crop of oats was growing. Potter and Snyder (17) working on field soils found the CO_2 to vary ten-fold in a few days on some of the plots studied. The writer has not attempted a comprehensive review of the studies of carbon dioxide in the soil-air, but only enough to show its probable range and consequent relations to the soil-solution and the calcium carbonate dissolved in it.

Changes in soil-temperatures will vary the proportion of CO_2 present, because the respiration of plants varies with the temperature in accordance with the principle of acceleration of chemical action by heat.

The CO_2 in the soil-solution will be quickly affected by the changes in the soil-atmosphere for Johnston (10) states that electrical conductance shows the establishment, within ten minutes, of equilibrium between the CO_2 of the air and an unstirred solution in an open beaker.

The concentration of carbon dioxide in the soil-solution varies with the proportion in the atmosphere, the temperature of the soil and the amount of salts in the solution. The coefficient of solubility decreases as the temperature rises and as the salt content increases; but in accordance with Henry's Law it remains constant when variations occur in the pressure of the gas above the solution. Solubility data for carbon dioxide in water and in salt-solutions have been determined by Just (12), Geffcken (6) and others, and their results have been compiled by Seidell (20) and by Cameron and Bell (2).

The mathematical relations between the carbon dioxide of the atmosphere and the calcium carbonate in the solution that is in contact with it, have been clearly discussed by Johnston (9) and also by Stieglitz (23). Several equations are required for their expression.

The solubility of CO_2 is usually expressed in terms of liters of the gas, reduced to 0°C. and 760 mm., dissolved in one liter of the solvent. Since a gram-molecule of a gas normally occupies 22.4 liters, the solubility factor for CO_2 at a given temperature divided by 22.4 gives the molar concentration of the solution at that temperature. This constant, c, multiplied by the partial pressure, P, of CO_2 in the atmosphere, will give the molar concentration of CO_2 in the solution in contact with the atmosphere. By P is understood the fraction by volume of CO_2 in one atmosphere. It is assumed in such a calculation that all of the dissolved CO_2 is transformed into H_2CO_3. This is probably not the fact; but since the proportion transformed cannot be ascertained experimentally, the assumption is the best that can be made. We have then as the equation for the relation between the carbon dioxide of the air and the carbonic acid of the solution,[2]

$$[H_2CO_3] = cP \qquad (1)$$

There are also required the equations for calculating the equivalent ion concentrations of the carbonic acid.

$$\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = k_1 \qquad (2)$$

$$\frac{[H^+] \times [CO_3^-]}{[HCO_3^-]} = k_2 \qquad (3)$$

[2] Brackets around a formula signify the molar concentration of the substance thus represented.

Since $CaCO_3$ is difficultly soluble and its saturated solution a dilute one, the equation for the solubility-product of calcium carbonate completes the required number for demonstrating the solubility of $CaCO_3$ in the soil solution.

$$[Ca^{++}] \times [CO_3^-] = K \tag{4}$$

By algebraic methods, Johnston (9) derived from equations 1, 2 and 3 and the ionization equation for water, $[H^+] \times [OH^-] = Kw$, two other equations which express the relations of the ionic concentrations in terms of ionization constants and the molar concentration of CO_2. The evaluation of these equations was determined by him from the data produced by different workers,[3] $c = 0.0441$ in pure water at $16°C.$; $k_1 = 3.04 \times 10^{-7}$ at $18°C.$; $\frac{k_1}{k_2} = 5600$; $K = 0.98 \times 10^{-8}$; and $Kw = 0.5 \times 10^{-14}$ at $18°C.$ The required equations are now as follows:

$$[Ca^{++}] \times [CO_3^-] = K = 0.98 \times 10^{-8} \tag{4}$$

$$\frac{[HCO_3^-]^2}{[CO_3^-]} = \frac{k_1}{k_2} \times cP = 5600 \times 0.0441\,P = 247\,P \tag{5}$$

$$\frac{[OH^-]}{[HCO_3^-]} = \frac{Kw}{k_1 cP} = \frac{0.5 \times 10^{-14}}{3.04 \times 10^{-7} \times 0.0441\,P} = \frac{3.73 \times 10^{-7}}{P} \tag{6}$$

The dissolved $CaCO_3$ is transformed by the H_2CO_3 into $Ca(HCO_3)_2$ and by hydrolysis of Ca^{++} there is formed some $Ca(OH)_2$. The total ion equivalent of Ca^{++} is therefore $[Ca^{++}] = \frac{1}{2}[HCO_3^-] + [CO_3^-] + \frac{1}{2}[OH^-]$ which must be satisfied by the values obtained in the three equations above. (The HCO_3^- formed by the ionization of H_2CO_3 which is produced by hydrolysis as well as $Ca(OH)_2$ is not taken into account, since its numerical value is practically negligible.)

Johnston's (9) calculations from the data of Schloesing (19), have been used as the basis of the writer's determination of the solubility of $CaCO_3$ in the soil-solution. The complete solubility curve of $CaCO_3$ developed by Johnston and Williamson (11), was plotted by them with logarithms of the pressures of CO_2 as abscissae and the logarithms of $[Ca^{++}]$ as ordinates. The sector of this curve lying between $P = 0.0003$, the common proportion of CO_2 in country-air, and $P = 1.0000$, or pure CO_2 at atmospheric pressure, is practically a straight line. Upon a large graph of this sector, there were interpolated along the abscissa, the values of Log P showing the variations in the soil-atmosphere; there were then read off the corresponding ordinates or values of Log $[Ca^{++}]$, which were used in the equations as trial values. By trial and error methods

[3] The data of Bohr were the basis of the calculation of c; the value of k_1 determined by Walker and Cormack is generally accepted; the value of k_2 cannot be determined directly, and the ratio was calculated from the work of McCoy with $NaHCO_3$ and Na_2CO_3. His work was conducted at $25°C.$ but Johnston uses the ratio at other temperatures as no better data are available. Seyler and Lloyd claim that 7100 is a better value for the ratio which they obtained in their investigations. The value of K was calculated from solubility data obtained by Schloesing and by Engel.

the values could then be modified until all the equations were satisfied simultaneously.

Some of Schloesing's (19) data were at pressures of CO_2 within the range of the soil-atmosphere and Johnston's (9) values are therefore incorporated in table 1.

This table shows that for any pressure of CO_2 in the atmosphere, there is bound to be a definite concentration of calcium in the solution, principally as $Ca(HCO_3)_2$, provided there is solid $CaCO_3$ in contact with the solution.

Although the calculations have been made for pure water at a temperature of 16°, there is strong probability that the results may be representative of a large part of the growing season in the real soil-solution. The temperature of 16° is in the higher part of the range of soil-temperatures. The solubility of

TABLE 1

Concentration of ions of CaCO₃ in water at 16°C. in equilibrium with CO₂ at various pressures

P	[Ca^{++}]	1/2[HCO$_3$$^-$]	[CO$_3$$^=$]	[OH$^-$]	pH
*0.0003	0.000579	0.000561	0.000017	1.44×10^{-6}	8.44
*0.0005	0.000682	0.000661	0.000014	1.00×10^{-6}	8.30
0.0010	0.000853	0.000842	0.000011	0.63×10^{-6}	8.10
0.0020	0.001072	0.001063	0.000009	3.96×10^{-7}	7.89
*0.0033	0.001222	0.001214	0.000008	2.80×10^{-7}	7.74
0.0050	0.001451	0.001444	0.000007	2.14×10^{-7}	7.63
0.0100	0.001826	0.001820	0.000006	1.35×10^{-7}	7.43
*0.0138	0.001945	0.001940	0.000005	1.12×10^{-7}	7.35
0.0150	0.002091	0.002086	0.000005	1.03×10^{-7}	7.31
0.0170	0.002180	0.002175	0.000005	0.95×10^{-7}	7.28
0.0200	0.002296	0.002291	0.000005	0.93×10^{-7}	7.26
0.0250	0.002477	0.002472	0.000005	0.74×10^{-7}	7.16
*0.0282	0.002541	0.002537	0.000004	0.67×10^{-7}	7.12
0.0334	0.002726	0.002722	0.000004	0.61×10^{-7}	7.08
*0.0500	0.003048	0.003045	0.000003	0.47×10^{-7}	6.97
*1.0000	0.008440	0.008440		0.31×10^{-8}	5.80

* From Johnston's table calculated from Schloesing's data.

CO_2 in water increases as the temperature falls, hence should be greater during a large part of the growing season. The soluble salts in the soil-solution, according to the writer's observation, are generally below a total concentration of 0.1 N calculated in terms of [NaCl] and will reduce the solubility of CO_2 slightly. Respiration of plant-organs in the soil decreases with lowering temperature and will more or less offset the increased solubility of CO_2 in the solution by lessening the pressure in the soil-air at the lower temperatures.

To transform the ion concentrations [Ca^{++}] into the equivalent expression of $CaCO_3$ in parts per million of solution, there is required the degree of ionization for each concentration. Since there were no conductivity data for calcium carbonate, Johnston (9) used the data for calcium acetate as a salt closely similar to calcium bicarbonate which forms the principal compound in the

solution. The carbonate and hydroxide are undoubtedly completely ionized.
By interpolation on a large scale graph, the degrees of ionization for the different
concentrations of $[Ca^{++}]$ were obtained with reasonably close approximation.
In table 2 are presented the solubility of $CaCO_3$ in parts per million by means
of the calculations.

The solubility of $CaCO_3$ in water in contact with air containing 0.00032
part of CO_2 has been measured by Wells (27) at temperatures ranging from
0° to 30°, showing a steady decrease from 81 parts per million at 0° to 52 parts
at 30°C.   Johnston and Williamson (11) calculated the value of c at the different
determinations, and demonstrated the decrease in molar concentration of H_2CO_3
with rise in temperature.

TABLE 2

Pressures of CO_2 and corresponding solubility of $CaCO_3$ in parts per million of solution

P	Ca^{++}	IONIZATION	Ca	$CaCO_3$
			moles	*p.p.m*
*0.0003	0.000579	0.915	0.000631	63.1
*0.0005	0.000682	0.912	0.000746	74.6
0.0010	0.000853	0.899	0.000948	94.8
0.0020	0.001072	0.895	0.001198	119.8
*0.0033	0.001222	0.890	0.001372	137.2
0.0050	0.001451	0.885	0.001640	164.0
0.0100	0.001826	0.875	0.002086	208.6
*0.0138	0.001945	0.870	0.002231	223.1
0.0150	0.002091	0.867	0.002412	241.2
0.0170	0.002180	0.865	0.002521	252.1
0.0200	0.002296	0.862	0.002664	266.4
0.0250	0.002477	0.857	0.002890	289.0
*0.0282	0.002541	0.856	0.002965	296.5
0.0334	0.002726	0.850	0.003207	320.7
*0.0501	0.003048	0.844	0.003600	360.0
*1.0000	0.008440	0.778	0.010850	1085.0

* From Johnston's table.

A study of the solubility of $CaCO_3$ in lysimeters, made by MacIntyre (14),
is corroborative of the theoretical principles of this discussion.   Three lysimeters
containing about 8 inches in depth of soil, were treated with large quantities
of $CaCO_3$ in the proportions of 8 tons, 32 tons and 100 tons per acre of surface.
The drainage waters were collected for four successive years, and the total
calcium determined in them and calculated as $CaCO_3$.   The results in grams
per liter of water are given in table 3.

The average concentration for the last two years is about 125 parts per mil-
lion. It is clearly seen that the solubility was independent of the quantity of
$CaCO_3$ in the soil, which is of course due to the constant presence in all of them
of solid $CaCO_3$.   In the first year, some of the calcium carbonate was undoubt-
edly transformed into nitrate, sulfate and chloride; but by the third and fourth

years, it is reasonably sure that the solubility was essentially in the form of bicarbonate. The rate of solubility in these later years corresponds to a low percentage of CO_2 in the soil-air, which would naturally be the condition in a soil with no vegetation growing in it.

The pH values in table 1 were derived from the values of [OH⁻] obtained by equation 6, by using the equation for the ionization of water, which may be written $\dfrac{1}{[H^+]} = \dfrac{[OH^-]}{Kw}$ from which we get $Log\,\dfrac{[OH^-]}{Kw} = Log\dfrac{1}{[H^+]} = pH$. The value of pH may also be obtained from equation 2 which can be transformed into $\dfrac{1}{H^+} = \dfrac{HCO_3^-}{k_1cP}$. Therefore $Log\,\dfrac{1}{[H^+]} = Log\,\dfrac{[HCO_3^-]}{k_1cP} = pH$. This latter equation shows that with a change in P, the pressure of CO_2, there must be a change in the value of pH. An increase in CO_2 will lower the value of pH, that is, the alkalinity is lessened.

In the absence of other salts, the presence of $CaCO_3$ in the soil will insure a reaction on the alkaline side of neutrality within the ordinary range of CO_2 found in the soil-atmosphere, but the value of pH cannot rise above the value for the solution in contact with the free air.

TABLE 3

Leaching of $CaCO_3$ from soil expressed in grams per liter of drainage water

CaCO₃ IN SOIL	1914–15	1915–16	1916–17	1917–18
tons	*gm.*	*gm.*	*gm.*	*gm.*
8	0.4285	0.1615	0.1250	0.1187
32	0.3643	0.1570	0.1275	0.1232
100	0.4232	0.2175	0.1265	0.1313
Average.........	0.4053	0.1887	0.1263	0.1244

THE EFFECT OF SOLUBLE SALTS ON THE SOLUBILITY OF $CaCO_3$ IN EQUILIBRIUM WITH CO_2

In common fertilizer practice there are applied to the soil phosphates of calcium; sulfates, nitrates and chlorides of potassium, sodium, calcium and magnesium; and sulfate of ammonia. The calcium salts have an ion in common with the calcium carbonate and may be expected to depress its solubility. The salts of potassium, sodium, magnesium and ammonia have no ions in common with $CaCO_3$ and therefore tend to increase its solubility.

The extent of their influence on the soil-solution in the presence of a reserve of $CaCO_3$ is of much interest and it is possible to indicate it approximately. The experimental data are however scarce and their use is of more value qualitatively than otherwise.

Stieglitz (23) has discussed the theory of the action of $CaSO_4$ on $CaCO_3$ at considerable length. His outline is followed here; but with new data.

Since $CaSO_4$ is a difficultly soluble salt, its saturated solution will have a definite solubility-product constant in accordance with the equation

$$[Ca^{++}] \times [SO_4^-] = K^1$$

Harkins and Paine (8) have determined the ion concentration and solubility-product of a saturated solution of $CaSO_4$ at 25°.

$$[Ca^{++}] = [SO_4^-] = 0.015816 \text{ and } K^1 = (0.015816)^2 = 2.503 \times 10^{-4}$$

According to Stieglitz, in a solution saturated simultaneously with $CaCO_3$ and $CaSO_4$, the value of the ion concentration of calcium in the solution would be expressed by both solubility-product equations, viz.,

$$[Ca^{++}] \times [CO_3^-] = K$$
$$[Ca^{++}] \times [SO_4^-] = K^1$$

At 25°, Johnston and Williamson (11) have calculated the value of K to be 0.87×10^{-8}.

The proportion of sulfate ions to carbonate ions is expressed by the ratios

$$\frac{[SO_4^-]}{[CO_3^-]} = \frac{K^1}{K} = \frac{2.503 \times 10^{-4}}{0.87 \times 10^{-8}} = 28770$$

Therefore there is about 28,000 times as much sulfate as there is carbonate in solution simultaneously at 25°, and for a preliminary calculation it is assumed that the ion concentration $[Ca^{++}]$ is wholly from the $CaSO_4$ and is 0.015816. If the solubility-product K, 0.87×10^{-8}, is divided by 0.015816, there is obtained the maximum value for the ion concentration $[CO_3^-] = 0.55 \times 10^{-6}$.

Using the equation for the concentration of bicarbonate and carbonate in equilibrium with the CO_2 of the air, which is

$$\frac{[HCO_3^-]^2}{[CO_3^-]} = \frac{k_1}{k_2} \times cP$$

we may for convenience write it in the form

$$[HCO_3^-] = \sqrt{\frac{k_1}{k_2} \times cP \times [CO_3^-]}$$

The value $\frac{k_1}{k_2}$ is still maintained at 5600, but at 25° the value of c is 0.0338.

The CO_2 pressure P may be any pressure within the range of soil-air. Taking the highest value mentioned by Turpin (24), 0.0334, and the maximum value obtained for $[CO_3^-]$ in the presence of $CaSO_4$, the above equation becomes

$$[HCO_3^-] = \sqrt{5600 \times 0.0338 \times 0.0334 \times 0.55 \times 10^{-6}}$$
$$[HCO_3^-] = 0.001865$$

The bicarbonate ions are twice as numerous as the calcium ions, hence $[Ca^{++}]$ from the dissolved bicarbonate[4] will be 0.000932.

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[4] It must be kept in mind that these calculations are only approximations that serve to show the direction of the reactions.

The degree of ionization of calcium acetate of equivalent concentration is 0.90 and the molar concentration of $CaCO_3$ will be 0.00103, or 103 parts per million of solution.   The presence of $CaSO_4$ has theoretically lowered the solubility of $CaCO_3$ under the conditions from about 300 parts per million to 100 parts per million.

The effect of the $CaSO_4$ on the reaction of the solution can be shown by using the equation for the value of pH, viz.,

$$\frac{1}{[H^+]} = \frac{[HCO_3^-]}{k_1 \, cP} = \frac{0.001865}{3.04 \times 10^{-7} \times 0.0338 \times 0.0334}$$

$$\text{Log} \frac{1}{[H^+]} = 6.63 = pH$$

The value of pH has been changed from 7.08 to 6.63 or from neutrality to acidity in this particular case.

The lowering of the value of pH can easily be seen qualitatively by shaking two solutions, one of water with solid $CaCO_3$ alone and the other with both solid $CaCO_3$ and solid $CaSO_4$.   On adding an indicator, preferably cresol red, there will be noticeable a marked depression of the pink tint in the solution containing $CaSO_4$.

Land plaster or gypsum may have value at times in reducing the alkalinity of a soil-solution for some crops, when the presence of $CaCO_3$ is a disadvantage, as in cases of potato scab and some root rots.

The effect of phosphates of calcium on the solubility of $CaCO_3$ should be similar to the action of $CaSO_4$ because there is the common ion Ca^{++} and the dicalcic as well as the tricalcic phosphate is a difficultly soluble salt in water, so there may also be a saturated solution with respect to it in the soil at times. Cameron and Seidell (4) in a study of the solubility of these phosphates used solutions saturated with CO_2 at atmospheric pressure in contact with both the solid phosphate and solid $CaCO_3$ at 25°.   Their results were as follows in total Ca dissolved and total PO_4.

	CALCIUM	PHOSPHATE
40 gm. $Ca_3(PO_4)_2$ per liter................................	0.3060 gm.	Trace
40 gm. $CaHPO_4$ per liter................................	0.3130 gm.	0.0810 gm.

In the first case the molar concentration, [Ca], was 0.00765 and in the second it was 0.00782, from both phosphate and carbonate.   The phosphate concentration was not estimated in the first but in the second case it was [PO_4] = 0.00085, one-half of which subtracted from 0.00782 leaves 0.00740 as [Ca] from carbonate in solution, assuming that the dicalcic phosphate is transformed into the monocalcic by the carbonic acid.   For a comparison with the solubility of $CaCO_3$ alone in water saturated with CO_2 at atmospheric pressure we turn back to table 2 where the molar concentration [Ca] is 0.01085 at 16°.   Since

the solubility-product constants at 16° and 25° are respectively 0.98×10^{-8} and 0.87×10^{-8}, we can estimate the molar concentration at 25° to be approximately in the ratio of 87 to 98, hence $0.01085 \times \frac{87}{98} = 0.00963$ which is a higher concentration than the molar concentration in the presence of either of the calcium phosphates. Therefore what slight data we have show an agreement with the solubility laws for dilute solutions. Since a depression of the $[HCO_3^-]$ causes at the same time a lowering of the numerical value of pH, we see that phosphates of calcium should lessen the alkaline effect of $CaCO_3$ to a small extent.

Salts of potassium, sodium and magnesium which occur in fertilizer, are the chlorides, sulfates and nitrates. They have no ions in common with the $CaCO_3$ and should in dilute solutions, increase the solubility of the solid $CaCO_3$, in accordance with the established principles of solubility. Numerous experiments have been recorded of solutions with high concentrations of the various salt mentioned; but scarcely any data have been found at concentrations similar to a soil-solution where the soluble salts seldom reach a concentration of 0.1 normal. Cameron and Seidell (4) studied the effects of NaCl and Na_2SO_4 in which they used one or two concentrations approximating this low limit. The solutions were in equilibrium with atmospheric air, which was probably the air of the laboratory, because the solubility of the $CaCO_3$ in the water alone was much higher than any results obtained in known cases of open air and differ with the two experiments. The solutions were in contact with solid $CaCO_3$ at 25° for 35 days or more.

The solubility was expressed in terms of $Ca(HCO_3)_2$. NaCl increased the solubility from 0.1046 gm. in pure water to 0.1770 gm. per liter with the salt and Na_2SO_4 increased it from 0.0925 gm. to 0.2330 gm. per liter.

No data have been found involving solutions in which potassium and magnesium salts were used in equilibrium with CO_2 in air, but in pure water Cameron and his co-workers found that these salts increased the solubility of $CaCO_3$ more than was effected by sodium salts under equal conditions.

Harkins and Paine (8) have shown that 0.02 N and 0.1 N KNO_3 increased the solubility of $CaSO_4$ from the equivalent concentration 0.0306 in water alone to the equivalent 0.0482 in the highest concentration of salt. Brönsted and Petersen (1) have also shown that dilute solutions of potassium, sodium and magnesium salts cause positive increases in the solubilities of an extensive series of difficultly soluble salts containing no ions in common. It is reasonably sure that in the soil, the solid $CaCO_3$ which may be present, will have its solubility increased by the application of fertilizers containing salts with no ions in common with it.

We may also consider that any increase in the solubility of $CaCO_3$, which is a salt of a strong base and a weak acid, necessarily produces by hydrolysis more increase in hydroxyl ions than in hydrogen ions.

Therefore the effect of fertilizer salts, $NaNO_3$, KCl, K_2SO_4, etc., will be to increase the numerical value of pH, that is, the alkalinity of the soil-solution, if $CaCO_3$ is present.

The effect may be shown qualitatively by a simple experiment. Finely powdered $CaCO_3$ is added to several open flasks containing respectively equal volumes of water, 0.1 N KCl, 0.1 N NaNO$_3$ and 0.1 N KCl + NaNO$_3$. To each solution is added the same measure of an indicator, either cresol red or thymol blue. When the solutions reach equilibrium, the alkaline effects of the added salts are noticeable. It may be partly a "salt effect" on the indicator; but the low concentration of the salt and the character of the indicators used, should render such an effect nearly negligible. Furthermore, soil-extracts have shown similar comparative tints as mentioned later, whatever the cause.

Ammonium salts, of which ammonium sulfate is most commonly used in fertilizers, differ somewhat in their effects on $CaCO_3$ in solution, from the salts of potassium and sodium. Ammonium compounds are salts of a weak base and a strong acid, or the opposite of $CaCO_3$, which is a salt of a strong base and weak acid.

The metathesis is represented by the reaction

$$Ca(HCO_3)_2 + (NH_4)_2SO_4 \rightleftharpoons CaSO_4 + 2NH_4HCO_3.$$
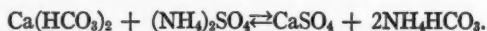
The results are a neutral salt of difficult solubility and a salt readily hydrolyzed and dissociated into a weakly ionized base and acid. The first effect is to dissolve $CaCO_3$ by forming the more soluble $CaSO_4$, while the formation of H_2SO_4 by hydrolysis of the ammonium salt produces an acid reaction of the solution. When equilibrium is finally reached, if enough $CaSO_4$ is formed to make a saturated solution, the result is closely like that of adding solid $CaSO_4$ to the solution containing $CaCO_3$.

There are no numerical data that can be used to demonstrate this line of action, but indicators with appropriate ranges show the changes in pH values very strikingly by their varying tints.

The action of the soluble salts on $CaCO_3$ and on the reaction of the soil are to widen the range of pH values beyond the limits of $CaCO_3$ alone. Salts of sodium and potassium tend to raise the pH values while calcium and ammonium salts depress them.

This discussion of the application of solubility laws to the action of calcium carbonate in soils has been given as a preliminary to the discussion of results obtained with different fertilizers which have been applied to the plots used in the field experiments at the Massachusetts Agricultural Experiment Station.

THE RELATION OF SOLUBILITY LAWS TO THE FERTILIZERS USED ON THE PLOTS OF FIELD A

The plots of Field A, one of the experimental fields of the Massachusetts Agricultural Experiment Station have received a continuous fertilizer treatment since 1889. The field and its treatment have been repeatedly described in the publications of the Experiment Station, the latest one being by the writer (15).

The scheme of fertilization is shown in the diagram. Four plots lie between 1 and 6 in the field.

Diagram of Fertilizer Plots

1		6	7		8
SW	NW	W	SW	NW	W
Limed	Limed	Limed	Limed	Limed	Limed
1898	1898	1898	1898	1898	1898
1905	1905	1905	1905	1905	1905
	1919			1919	1919
Limed	Limed	Limed	Limed	Limed	Limed
1898	1898	1898	1898	1898	1898
1905	1905	1905	1905	1905	1905
1909	1909	1909	1909	1909	1909
1913	1913	1913	1913	1913	1913
	1919			1919	1919
SE	NE	E	SE	NE	E

1	6	7	8
NaNO$_3$	(NH$_4$)$_2$SO$_4$	No N	(NH$_4$)$_2$SO$_4$

Dissolved bone black and muriate of potash on all plots.

Quantities of fertilizer used annually, per acre:	Quantities of lime applied per acre:
Dissolved bone black............ 500 lbs.	1898........................... 2000 lbs.
Muriate of potash............... 250 lbs.	1905........................... 2000 lbs.
Nitrate of soda.................. 300 lbs.	1909........................... 5000 lbs.
Sulfate of ammonia............. 225 lbs.	1913........................... 4000 lbs.
	1919........................... 2000 lbs.

It will be noted from the diagram that all the plots have received calcium superphosphate in the form of dissolved bone black or dissolved rock phosphate. The superphosphate is necessarily accompanied by the calcium sulfate produced in its manufacture. The other components of the soil solution vary with the different plots, and include muriate of potash, nitrate of soda and sulfate of ammonia.

All the plots have received calcium carbonate, or calcium compounds which would soon become carbonate as shown by MacIntyre (14). The quantities of lime and dates of application have been widely varied. It will be noted that parts of the plots have received no lime for 16 years, while others were heavily dressed 8 years ago, and still others sparingly dressed 2 years ago.

These variations are sufficient to test the regulatory action of CaCO$_3$ on the soil solution by a study of the solubility effects of the different fertilizers on the CaCO$_3$.

The determination of the hydrogen-ion concentration, or the pH value, is the easiest means of studying the solubility effects, and this method has been followed for several years in comparing the soil-extracts obtained from the various fertilizer combinations.

Soil-extracts were prepared by shaking 20 gm. of air-dry soil with 200 cc. of distilled water at frequent intervals during about 1 hour. The liquid mass was then poured into a 3-inch funnel which was fitted with a small paper filter, not over 7 cm. in size. The paper and a considerable portion of the funnel were soon filled with the soil, which served as the filtering medium. The object of this practice was to reduce the adsorbing surface of the paper to as small an area as possible and prevent the selective ion adsorption which is quite noticeable when a dilute solution is filtered through a large paper filter. The filtrate was in all cases returned to the filter and passed through a second time, and if turbid, the refiltering was continued until the extract was clear. Under these conditions, the soil-extract was practically a percolate from the soil, since the small paper support must have become a negligible factor in any adsorption effect.

Some interesting differences in the behavior of the different soils were noted as the filtrations were made. All the soils are a fine sandy loam, therefore there was no difficulty in finally getting a clear and generally a colorless solution. The more acid the soils, the more freely they filtered and their extracts were like spring-water. The more alkaline the soils, the slower was the filtration and in some instances the extracts were slightly tinted.

In the measurement of pH values, colorimetric methods alone have been used. The earlier determinations were made with the indicators classified by Sörensen (22), and the standard buffer solutions recommended by Walpole (25). During the past two years, however, the solutions and indicators described by Clark (5) have been substituted with improved results. Bromcresol purple and bromthymol blue have replaced paranitrophenol and rosolic acid. Bromcresol purple gives much more brilliant gradations than paranitrophenol, and the changes of bromthymol blue are more readily matched than the tints of rosolic acid.

Precautions were steadily added as their necessity became apparent. The same glassware, especially, was used as nearly continuously as possible, in order to guard against variations in the solubility of the glass.

Gillespie (7), Sharp and Hoagland (21) and Knight (13) have very clearly shown the troubles and difficulties attending the study of pH values in soils.

The practice outlined gave consistent results each season, in the relative standing of the different soils studied; but the final combination of solutions and indicators gave slightly but positively higher pH values in all of the soils which contained $CaCO_3$.

The investigation during 1917 and 1918 was in the nature of an exploration. Samples were taken at irregular intervals and not simultaneously from all the plots. In 1919, other duties prevented any systematic work in the laboratory, but study of the results and of the literature caused a resumption of the work in the fall of 1920 and led to the systematic study of soil-extracts from the different plots throughout 1921.

The continuous presence of $CaCO_3$ in the soils throughout the study was shown by the behavior of the soil-extracts when concentrated in platinum dishes. The solution from the most heavily and the recently limed soils invariably increased in alkalinity toward rosolic acid and in most cases turned phenolphthalein pink. The increased hydrolysis of $Ca(HCO_3)_2$ by heat should produce such a result.

The results obtained in 1921 are given in table 4.

TABLE 4

Hydrogen-ion concentration in soil-extracts, 1921

	MAY 3	MAY 18	JUNE 24	AUGUST 6	SEPTEM-BER 2
	pH	pH	pH	pH	pH
Areas limed in 1898, 1905, 1909, 1913, and 1919					
1 NE..	7.4	7.4	7.3	7.3	7.6
7 NE..	7.1	7.0	7.2	7.1	6.9
8 E...	6.6	6.5	6.6	6.8	6.7
Areas limed in 1898, 1905, 1909, 1913					
1 SE..	7.1	7.2	7.1	6.9	7.4
6 E...	6.3	6.2	6.0	6.2	6.4
7 SE..	6.7	6.7	6.8	6.5	6.7
Areas limed in 1898, 1905 and 1919...............					
1 NW..	6.8	6.9	6.8	6.7	7.0
7 NW..	6.3	6.2	6.5	6.1	6.4
8 W...	5.3	5.4	5.6	5.7	5.8
Areas limed in 1898 and 1905....................					
1 SW..	6.5	6.3	6.4	6.4	6.8
6 W...	4.5	4.5	4.6	4.5	4.8
7 SW..	5.7	5.5	5.7	5.9	5.8

In the fertilizer scheme shown in the diagram, it will be noted that the whole field received a uniform quantity of dissolved phosphate. According to Cameron and Seidell (4), the monocalcium phosphate hydrolyzes to dicalcium phosphate and in the presence of $CaCO_3$ there would soon be in the soil only the difficultly soluble phosphates of calcium.

The amount of dissolved phosphate employed equivalent to 80 pounds of phosphoric pentoxide, P_2O_5, per acre may be assumed to be contained in the upper layer of soil that is stirred by the harrow, when the fertilizer is first applied. The same is equally true of the other chemicals used. According to this assumption, the material is mixed with approximately 1,000,000 pounds of soil, allowing 3,000,000 pounds per acre foot. At any rate, for convenience we may take this amount as the minimum quantity of soil in which the fertilizer is held.

The amount of soil-moisture which may be present will naturally vary widely. A convenient proportion for calculation and one that is reasonably apt to be present is 10 per cent. By these assumptions we have 100,000 pounds of water per acre in which to dissolve the different fertilizers.

If all the phosphoric pentoxide were dissolved in the soil water, there would be 0.8 part in 1000 parts of water.   The equivalent concentration [PO$_4$] would be 0.01126.   Cameron and Seidell (4) secured a concentration of only 0.00085 in a solution in contact with solid CaCO$_3$ and saturated with carbonic acid, therefore there is no doubt about the soil-solution being saturated with the difficultly soluble calcium phosphates soon after a dissolved phosphate is added to a limed soil.   The slight solubility of these calcium phosphates renders their possible effects on the reaction of the soil-solution very small.

Besides 0.8 part P$_2$O$_5$ in 1000 parts of soil-water, the application of the dissolved phosphate will add 1.5 parts CaSO$_4$.   The soil-solution will not be saturated with this salt, because a saturated solution contains over 2 parts of CaSO$_4$ in 1000 at any probable soil-temperature.   Nevertheless, the effect of the dissolved phosphate will approach that of an application of CaSO$_4$ in lowering the solubility of the CaCO$_3$ and lessening its alkaline effect.

The other fertilizers vary with the different plots, and will be considered individually.

Potassium chloride and sodium nitrate are used simultaneously on plot 1. This plot has shown the highest value for pH consistently throughout the study, especially where lime has been applied.   Both these salts are without any ions in common with each other or with CaCO$_3$.   Their possible equivalent concentrations in 10 per cent moisture are respectively [KCl] = 0.033 and [NaNO$_3$] = 0.035, which are the maximum concentrations practically possible if the fertilizer chemicals were pure salts.   There are no data on which to base any calculations of their probable quantitative effect; but they should each increase the solubility of the CaCO$_3$ and this is apparently true because plot 7 with KCl and without NaNO$_3$ is consistently less alkaline than plot 1.

Ammonium sulfate was employed on plots 6 and 8 under the same conditions with respect to the dissolved phosphate and potassium chloride.   The applications of lime have been varied.

If the ammonium sulfate were to react with the CaCO$_3$ until all its SO$_4$ had combined with Ca, the result in conjunction with the CaSO$_4$ from the dissolved phosphate would produce a solution saturated with CaSO$_4$.   There is no experimental evidence that such a complete interchange occurs and equilibrium probably is established with some ammonium sulfate still unchanged, although the proportion may be small.   The depression of the solubility of CaCO$_3$ is sufficient to lower the pH value below that of the other plots, which is consistently the relative position each season.

It will be noted that the pH values, while following the order of values for the solubility of CaCO$_3$ and the different salts in pure water, are nevertheless uniformly lower in numerical quantities.   This is probably due to the dilution by the extraction process.   On the other hand the ten-fold dilution invariably used is not an accurate measure of the original solution, because some solubility of difficultly soluble soil-compounds will take place.

It has been invariable that concentration in platinum dishes of the soil extracts from the limed soils increases the pH values. In the extracts from plots 1 and 7, they more or less quickly beome pink to phenolphthalein, while the extracts from plots 6 and 8 usually show alkalinity only to rosolic acid or bromthymol blue. This intensification of the alkalinity is partly due to expulsion of CO_2 in solution and partly to the increased hydrolysis of the $CaCO_3$ at the higher temperature. Such an intensification of the alkaline tints of indicators is strong evidence of the presence of $Ca(HCO_3)_2$ in solution and its consequent occurrence in the soil.

On the areas which have received no lime since 1905, 1 SW, 6 W, and 7 SW, there are several indications that $CaCO_3$ has been practically all removed. The extracts from these soils show bare traces of turbidity to ammonium oxalate, which might be attributed with good reason to the $CaSO_4$ of the superphosphate.

In the absence of $CaCO_3$, the application of superphosphate may result in the formation of $AlPO_4$ and $FePO_4$ in addition to the tri- and di-calcium phosphates. These are all difficultly soluble salts and can affect the soil-extracts very slightly (3).

The solubility effect of ammonium sulfate is very striking under these conditions as manifested on plot 6 W.

Its action is susceptible of explanation. It is a salt of a weak base and a strong acid and consequently hydrolyzes with the formation of NH_4OH and H_2SO_4. The H_2SO_4 has a much higher degree of ionization than the NH_4OH, and the solution of $(NH_4)_2SO_4$ is therefore positively acid in its reaction. The amount hydrolyzed can be calculated by the formula for the degree of hydrolysis. The possible equivalent concentration is 0.034 N which is closely like that of KCl and $NaNO_3$ in the other plots.

The equation for the degree of hydrolysis (26) of a salt with a weak base and a strong acid is for approximate calculations $\dfrac{h^2 C_a}{1-h} = \dfrac{K_w}{K_B}$. The degree of hydrolysis sought is h, the concentration of the solution is C_a, while K_w and K_B are the ionization constants of water and the weak base, which in this case is ammonia. We would have on substituting numerical values (16).

$$\frac{0.034\ h^2}{1-h} = \frac{0.5 \times 10^{-14}}{1.72 \times 10^{-5}} \text{ at } 18°$$

which is the experimental temperature nearest the soil-temperatures.

The equation is a quadratic one and when ready for the final solution becomes for our purpose

$$h = \sqrt{\frac{0.5 \times 10^{-14}}{0.034 \times 1.72 \times 10^{-5}}}$$

The degree of hydrolysis is 0.00009 which applied to the concentration 0.034 N gives a concentration of H_2SO_4 of 0.000003 N. This concentration may be

considered completely ionized, or $\frac{1}{2}$ [SO$_4$=] = [H+] = 3 × 10^{-6}. The Log $\frac{1}{[H^+]}$ = 5.5 = pH. This is closely approximated by a solution of ammonium sulfate of this strength with methyl red as an indicator.

Numerous analyses of soil-extracts from these plots have shown that in the absence of lime there occur sulfates of aluminum, iron and manganese. The two former salts hydrolyze even more completely than ammonium sulfate. The ionization constants of these weak bases are unknown, hence their degree of hydrolysis cannot be estimated by the formula; but their pH values are 4 or less. Concentration of these soil-extracts increases their acidity intensity very noticeably toward indicators.

Like the extracts from the more recently limed areas, these appear to be diluted soil-solutions when their theoretical acidity is considered. Nevertheless, there is ample evidence that no reserve of CaCO$_3$ is present in this area but that it has been removed owing to the solubility of CaSO$_4$.

The pH values found for the soil-extracts from 7 SW, appear to be due mainly to the absence of any calcium bicarbonate in the solutions, and the consequent rapid esablishment of equilibrium with the CO$_2$ in the atmosphere of the laboratory. It has been demonstrated that a solution saturated with bicarbonate at a high partial pressure of CO$_2$, changes very slowly toward equilibrium with a lower pressure of the gas. Two flasks containing water and solid CaCO$_3$ were set side by side open to the atmosphere. To both were added 10 drops of cresol red indicator, which produced practically equal tints in the two solutions. Into one flask was passed CO$_2$ until the indicator was of the deepest acid tint. Days elapsed before the indicator tints returned to equality in color. This is in marked contrast to the rapid equilibrium of a solution of carbonic acid alone, as noted by Johnston (10).

The absence of bicarbonates from the soil-extracts prepared from 7 SW, was shown when the extracts were evaporated in platinum dishes. As the concentration proceeded, the indicator either remained unchanged or turned slightly acid. If bicarbonate of calcium were present, the indicator should have turned toward alkalinity by the increasing hydrolysis of the base.

The calculated pH value of carbonic acid in water exposed to the atmosphere also compares closely with the values found in the soil-extracts. By use of equation 2 the approximate value of pH is obtained as follows:

$$\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = k_1 = 3.04 \times 10^{-7}$$

In a solution of carbonic acid, [H+] and [HCO$_3$$^-$] are equal, and [H$_2CO_3$] = cP. Therefore the equation becomes [H+]^2 = 3.04 × 10^{-7} × cP.

During the season of soil-extract examinations, the windows of the laboratory were open and as a rule the determinations were made before the open window. The value of cP is consequently assumed to be 0.0441 × 0.0003 and the equation

becomes $[H^+] = \sqrt{3.04 \times 10^{-7} \times 0.0441 \times 0.0003}$

$$\text{Log } [H^+] = -6.3022 \text{ and Log } \frac{1}{[H^+]} = 5.69 = pH.$$

This value is practically the same as those obtained in the extracts.

The value of H^+ varies proportionally to the square root of the pressure P of the CO_2 in the atmosphere. The acidity of the solution in the soil should be greater than that of the extracts because the CO_2 must be more concentrated.

The soil-extracts from 8 W yielded about the same pH values as 7 SW, and when they were evaporated they changed indicators toward acidity. This behavior indicates that the light application of lime to this area in 1919 has been neutralized.

The soil-extracts from 1 SW were less acid than those from 7 SW and when they were evaporated, the concentrated extracts turned indicators slightly alkaline. This indicates the presence of bicarbonate of calcium in small amount, which is hydrolyzed by the heat. The probable source of this bicarbonate after 16 years with no added lime, has not yet been clearly explained by our studies.

SUMMARY

When solid calcium carbonate exists in the soil in contact with the soil-solution, the concentration of calcium carbonate in the solution is dependent upon the amount of carbon dioxide in the soil-air and is independent of the amount of calcium carbonate in reserve.

When chemical fertilizers are used in addition to calcium carbonate, the application of calcium phosphates, calcium sulfate and ammonium sulfate lowers the concentration of calcium carbonate in the soil-solution and lessens its alkalinity. The addition of sodium nitrate and potassium chloride increases the concentration of the calcium carbonate and the alkalinity of the solution.

The soil-extracts obtained from the limed plots of Field A have given results in accordance with these principles.

The extracts obtained from the unlimed soils showed little effect by superphosphate and potassium chloride on the pH value. The addition of ammonium sulfate produced low pH values, as though sulfates of aluminum and iron were present. Sodium nitrate when added caused the extracts to behave as though calcium bicarbonate was present.

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ACID PHOSPHATE PRODUCTION BY THE LIPMAN PROCESS: III. THE USE OF GREENSAND MARL AS THE INERT MATERIAL IN BUILDING UP SULFUR-FLOATS MIXTURES[1]

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In discussing experiment 2 (4) it was pointed out that from a physico-chemical standpoint the accumulation of phosphoric acid and sulfuric acids in the initial stage of preparing culture is the logical step in building up concentrated composts. For that purpose greenhouse soil was used as a store house with fairly good results. Since the soil has been looked upon primarily as an inert material for the accumulation of acid it was deemed possible to substitute another material for this purpose. It is important that the added materials should contain no harmful ingredients and should favor the activities of the sulfur-oxidizing organisms. Experiments conducted with greensand marl for the purpose of studying the effect of sulfur oxidation on the solubility of the insoluble potassium compounds suggested this material. These experiments, reported elsewhere (1) showed that the hydrogen-ion concentration of mixtures of greensand marl and sulfur increased very rapidly. The phosphate content of the marls should favor the reaction in the proper direction, if readily available. Besides, the potassium content of the marls would aid to the fertilizing value of the mixtures. To test out this point experiment 5 was conducted.

EXPERIMENT 5. INITIAL STAGE

A mixture of 60 gm. of marl, 25 gm. of soil and 15 gm. of sulfur was made up, the moisture-content kept as in the previous experiments and the mixture was similarly inoculated and incubated. Table 1 gives the results of the experiment.

The data presented show that the insoluble phosphates in the marls are readily set free. At this point it seems appropriate to look into the possible reactions involved in the action of sulfuric acid on the insoluble silicates. It is well known that the feldspars are relatively insoluble in acids. Still, on prolonged continuous contact with acids the silicates are attacked, liberating silicic acid. The introduction of the tertiary phosphates into a medium of

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sulfuric and silicic acid might cause the following reactions. The tertiary phosphates might be attacked setting free calcium ions; these would have to unite either with the sulfate to produce gypsum or with the silicic acid to form calcium silicate. Calcium silicate has a smaller solubility product, or ionic product as it sometimes is called, than gypsum and would be precipitated. As a result the concentration of gypsum in solution would become negligible. The concentration of the potassium sulfates and phosphates would, of course, increase, but these do not have so inhibitory an effect on the microörganisms as gypsum has. The replacement process which plays such an important rôle in mineralogical considerations, may have an effect in the greensand marl mixtures. In accordance with these theoretical considerations the greensand marl mixtures were used as the base mixture instead of the greenhouse soil.

TABLE 1

Conversion of insoluble phosphates of marl composted with sulfur and soil

INCUBATION PERIOD	REACTION	SOLUBLE PHOSPHORUS PER GRAM OF MIXTURE	TOTAL P PER GRAM OF MIXTURE
days	*pH*	*mgm.*	*mgm.*
0	6.4	0.472	3.91
12	2.4	1.81	3.62
30	1.0	3.26	3.31

EXPERIMENT 6. SECOND AND THIRD STAGES

To the base mixture from experiment 5 a mixture of 100 gm. floats and 5 gm. sulfur was added. After 64 days, 91 gm. of floats alone was added, marking this point as the beginning of the third stage.

The interesting points to notice from the data are: first, the fact that in the second stage, after 5 days of incubation, the hydrogen-ion concentration reached the point where the primary phosphate makes its appearance, thus indicating a rapid conversion due to the activities of the sulfur-oxidizing organisms. At this time 33 per cent of the phosphates became soluble. This rapid rise may be explained by the accumulated acids in the initial stage, as may readily be seen from the pH of the mixture as given in table 2. Second, after 5.5 weeks free acid was accumulating again and reaction was coming fast to completion. Unfortunately, due to pressure of other work determinations were not made frequently enough to follow the reaction closely. As it was, the third stage was begun only after 9 weeks. The reaction as it may be noticed was slowing down. Still, after 44 days over 60 per cent of the total P_2O_5 content (almost 12 per cent) became available. If we compare the marl series of building up of the compost with that of the soil series (4) we might at first be inclined to think that better results were secured with the soil, especially if we compare culture 1 in table 3 (4) with the marl series. There the total incubation period is 17 weeks. The total P_2O_5 content was 13 per cent with 55 per cent of it available. In the marl series we have only a 12 per cent total and over 60 per

cent available, but the total incubation period is a little over 19 weeks. An analysis showed that all the sulfur had been oxidized; the culture, therefore, suffered from the lack of the driving force of the reaction. It is the author's opinion that upon repeating the series with slight modification the marl cultures might be in the lead. It should be recorded here that the marl mixtures were in a better physical condition than the soil mixtures.

TABLE 2

Course of conversion of insoluble phosphates into soluble form in the second and third stage of the Lipman process

INCUBATION PERIOD	REACTION	TOTAL P PER GRAM OF MIXTURE	SOLUBLE P PER GRAM OF MIXTURE	SOLUBLE PHOSPHORUS
		Second stage		
days	*pH*	*mgm.*	*mgm.*	*per cent*
5	2.8	23.3	7.8	33.0
38	2.2	22.6	16.2	73.0
64	1.8	....	22.08	100.0(?)
		Third stage		
0	3.4	54.9	17.4	32.0
44	2.8	51.38	31.29	60.9

EXPERIMENT 7

Course of conversion of soluble phosphates from a highly concentrated mixture to a less concentrated mixture

Sumultaneously with experiment 6 another experiment was performed with the idea of working backwards, i.e., beginning with a highly concentrated mixture and gradually diluting it with soil or marl. Mixtures were made up as indicated in table 3.

The mixtures were made up to the proper moisture-content as in the previous experiment and allowed to incubate.

Table 4 gives the results of the experiment.

The prolonged period of incubation necessary for the concentrated mixtures to reach the desired point of the reaction, namely a pH 2.8, makes this procedure an unpractical method. A step forward, however, must be recorded. In the earlier work of Lipman, McLean, Shedd, Rudolfs and those of the author of this paper, concentrated composts had to be abandoned. The only difference between their technique and that of the author was the appreciation of the moisture factor and the gain in weight of the cultures. In the cultures just described we find that number 1 had a total P_2O_5 content of 18 per cent with more than 42 per cent made available and number 6 had a total P_2O_5 content of 15 per cent with more than 50 per cent made available.

TABLE 3

Composition of various sulfur-floats cultures and additions made after 9 weeks of incubation

CULTURE NUMBER	FLOATS	SULFUR	GREENSAND MARL	GREENHOUSE SOIL	ADDITIONS MADE AFTER 9 WEEKS OF INCUBATION	
					Greenhouse soil	Greensand marl
	gm.	gm.	gm.	gm.	gm.	gm.
1	360	90	50	..	50	..
2	360	90	50	..	50	..
3	360	90	..	50	50	..
4	300	95	125	..	50	..
5	300	75	125	..	50	..
6	300	75	..	125	..	50

TABLE 4

Course of conversion of insoluble phosphates in the first and second stage in working down high concentrated mixtures to less concentrated

CULTURE NUMBER	AFTER 2 WEEKS' INCUBATION			AFTER 9 WEEKS' INCUBATION			AFTER 16 WEEKS' INCUBATION		AFTER 22 WEEKS' INCUBATION		AFTER 29 WEEKS' INCUBATION		
	Reaction	Total P per gm. of mixture	Soluble P per gm. of mixture	Reaction	Total P per gm. of mixture	Soluble P per gm. of mixture	Reaction	Soluble P per gm. of mixture	Reaction	Soluble P per gm. of mixture	Reaction	Total P per gm. of mixture	Soluble P per gm. of mixture
	pH	mgm.	mgm.	pH	mgm.	mgm.	pH	mgm.	pH	mgm.	pH	mgm.	mgm.
1	7.0	91.37	5.69	4.2	87.7	5.7	2.8	14.9	2.8	20.7	2.6	77.8	32.65
2	6.8	91.8	5.58	4.2	81.6	6.2	2.8	12.12	2.8	19.1	2.6	73.5	28.44
3	6.6	91.5	5.50	3.2	88.6	4.7	2.8	9.52	2.8	16.2	2.4	79.1	29.45
4	6.2	77.5	5.93	3.2	74.6	7.4	2.8	15.72	2.8	22.3	2.4	64.4	28.15
5	6.4	76.6	5.96	3.6	72.6	6.4	2.8	12.6	2.8	20.4	2.6	65.7	28.44
6	6.3	77.2	5.87	3.8	73.75	6.4	2.6	18.04	2.6	23.9	2.4	64.0	32.89

CONCLUSIONS AND SUGGESTIONS

The Lipman process of making acid phosphate by biological oxidation of sulfur seems to have practical possibilities. The best method of obtaining acid phosphate of a high total and also a high percentage of soluble phosphates is to start out with a dilute mixture and gradually build it up.

The suggestions which are to be made and, which the author hopes to try out if the opportunity will avail itself, are as follows:

1. Greensand marl should be used as the inert material for the initial stage with a small addition of soil rich in organic matter.

2. The sulfur content should be increased in the initial stage, thus making possible a larger accumulation of acid.

3. Simultaneously with the base mixture the second stage should be incubated and the sulfur content of this mixture should also be increased. This will appreciably cut down the time period in the second stage.

4. Only at the third stage should floats alone be added in an amount necessary to take care of the excess of sulfur added in the initial and second stages.

5. The moisture-content should be carefully kept up as given in the section on the effect of moisture content, as given in the first paper of this series (3).

6. Proper aeration should be provided for. If possible, mechanical aeration as outlined in the experiment on aeration (2) or something similar, should be practised.

7. The use of catalytic and stimulating agents found by McLean to be of value should be tried out, including some which were found by the author to be stimulating to *Thiobacillus thiooxidans* in culture solution, as reported (1).

8. A study should be made on the tolerance limits by the sulfur-oxidizing organisms to the salts found in a water extract of the mixtures.

It is the conviction of the author that, with proper handling, acid phosphate production by biological means may be accomplished on a practical basis. There is no doubt that a mixture with a total P_2O_5 content of 16 to 18 per cent of which 60 to 75 per cent or even more is available, could be made in three months.

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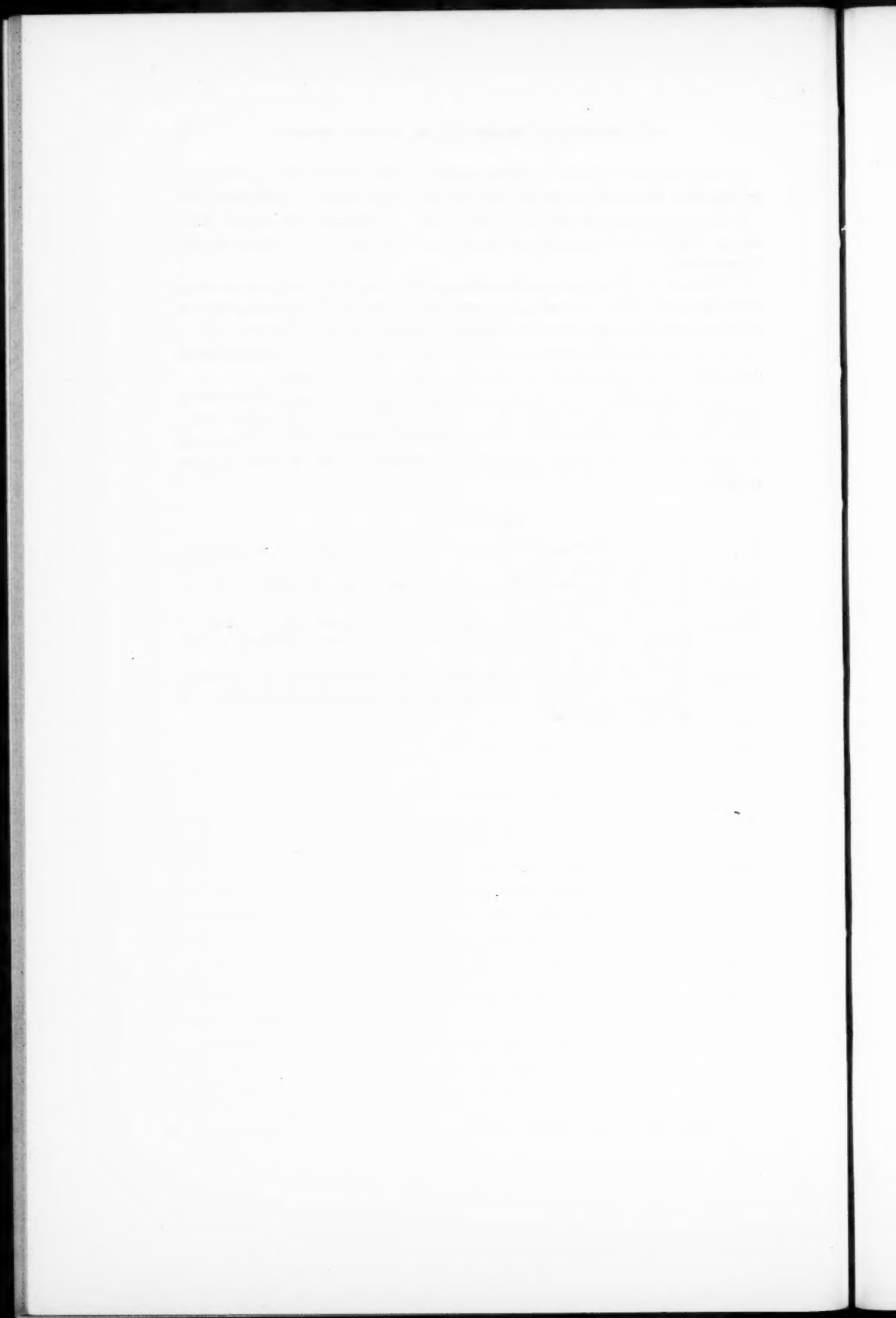
SOIL ACIDITY AS MEASURED BY SUGAR INVERSION, THE TRUOG TEST AND THE HYDROGEN-ION CONCENTRATION AND ITS RELATION TO THE HYDROLYSIS OF ETHYL ACETATE[1]

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It is generally recognized that acid soils contain soluble acids, as indicated by the hydrogen-ion concentration of the soil solution, and insoluble acids in the form of acid silicates and organic acids. There is need for a single measure of both of these forms of acids. The hydrogen-ion concentration is generally supposed to indicate the strength or degree of dissociation of the soluble acids and not the acidity of the insoluble or undissociated acids. However, it is probable that the hydrogen-ion concentration of most acid soils depends to a considerable extent on the amount and strength of the difficultly soluble acids in the soil. With this assumption, there should be a correlation between the hydrogen-ion concentration of the soil solution, the amount of sugar inverted by the soil and the degree of acidity indicated by the Truog test.

The sugar inversion method was studied because the rate of sugar inversion is generally considered to be a measure of the hydrogen-ion concentration. However, Rice and Osugi (7) and Osugi (4) reported that sugar inversion is influenced by the insoluble acids as well as by the hydrogen-ions in the soil solution. Other investigators (1) have advanced evidence to show that the catalytic effect of acids on the inversion of cane sugar is due partly to the hydrogen-ions and partly to the undissociated acid. The data of Rice and Osugi (7) show that the inversion of sugar is much greater in soil suspensions than in water extracts of the same soil. From later studies (4) Osugi concluded that the insoluble acid silicates in the soil suspension produce the greater part of the sugar-inverting power of acid soils. From this it appears that the sugar inversion method should give a good indication of soil acidity. Assuming that the hydrogen-ion concentration of the soil solution is influenced by the amount and strength of the insoluble acids, the results of the sugar inversion method should correlate fairly well with the hydrogen-ion concentration of the soil solution.

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[1] Published with the permission of the Director of the Wisconsin Agriculture Experiment Station.

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The Truog test (9) was included in this investigation because it is widely used as a practical test. Truog (8) has presented data showing that the degree of acidity indicated by this test is a resultant of the acidity and amount of the "active" soil acids. "Active" acids include all of the soluble and a considerable part of the insoluble acids. The results of this test should bear a fairly close relationship to the results of the sugar inversion method for the results of both methods are influenced by the soluble and insoluble acids. The Truog test should correlate fairly well with the hydrogen-ion concentration of the soil but the correlation between these two tests cannot be expected to be as close as the correlation between the results of the Truog test and the sugar inversion method.

Johnson (3) studied the relation between the hydrogen-ion concentration of fifty soils, the Veitch lime requirement and the degree of acidity indicated by the Truog test. He found very little relation between the Veitch lime requirement and the hydrogen-ion concentration. He states that the Truog method gave results which were a combination of the Veitch lime requirement and hydrogen-ion concentration.

EXPERIMENTAL

The acidity of forty-two soils was determined by the three methods mentioned above. The hydrogen-ion concentration was determined colorimetrically and electrometrically. At first some difficulty was experienced in getting the two methods to check satisfactorily. Later the difficulty was overcome. Only the results of the electrometric method are recorded in this paper. Readings of the electromotive force were made with an improved Leeds and Northrup potentiometer. Duplicate determinations agreed very closely and the results are accurate to pH 0.05. The hydrogen-ion concentration of the displaced soil solution (5) was found to be practically the same as that of a 1:2 water extract. This result does not agree with results secured by Plummer (6). He reported a higher hydrogen-ion concentration in the soil solution of an acid soil than in the water extract of the same soil.

The sugar inversion method was essentially the same as that used by Rice and Osugi (7). Fifty cubic centimeters of a 5 per-cent cane sugar solution were added to a flask containing 10 gm. of 20 mesh air-dry soil. The flasks were then placed in a water bath and a temperature of 80°C. maintained for three hours. During this time the flasks were frequently shaken to keep the soil in suspension. Upon removal from the water bath, distilled water was added to replace the small amount lost by evaporation. The suspension was then filtered and the invert sugar determined by titration. The results recorded are from single determinations. Duplicate determinations were made on several soils and the results agreed very closely.

The Truog test (9) was made in the usual manner.

The results secured with the three methods on twenty-three soils are given in table 1 and are shown graphically in figure 1. The soils are arranged in order of their acidity as indicated by the Truog test. It is at once evident that there is a good correlation between the results secured by the three methods. The correlation is best between the amount of sugar inverted and the acidity indicated by the Truog test. This is to be expected since the results of both methods are influenced by the quantity and strength of both the soluble and insoluble acids present. The hydrogen-ion concentration shows a very good relationship to the results of the other two methods. If

TABLE 1

Soil acidity as indicated by sugar inversion, the Truog test and the hydrogen-ion concentration

SOIL NUMBER	SUGAR INVERTED	HYDROGEN-ION CONCENTRATION	REACTION BY TRUOG TEST
	gm.	pH	
1	Trace	6.83	Very slight −
2	0.021	6.01	Very slight
3	0.017	5.72	Very slight +
4	0.017	6.67	Slight −
5	0.025	6.00	Slight
6	0.023	5.75	Slight
7	0.017	6.03	Slight +
8	0.033	6.15	Slight +
9	0.022	5.45	Slight ++
10	0.032	5.70	Medium −−
11	0.030	5.77	Medium −
12	0.045	5.23	Medium
13	0.043	5.14	Medium +
14	0.064	5.50	Medium ++
15	0.053	5.34	Medium ++
16	0.080	5.14	Strong −−
17	0.064	5.30	Strong −
18	0.110	5.16	Strong
19	0.127	5.22	Strong +
20	0.120	5.06	Strong +
21	0.133	4.73	Very strong −
22	0.186	4.85	Very strong +
23	0.350	4.32	Very strong +

soils of the same type and texture but with different field treatments are compared the results should correlate much better than when a large number of soils are selected without regard to type or texture.

In order to determine whether or not the correlation is better between soils of exactly the same type but having different field treatments, a second series of determinations was made. Nineteen soil samples, representing eight soils with two or more different field treatments were secured and the acidity determined by the three methods. The results are given in table 2 and graphically in figure 2.
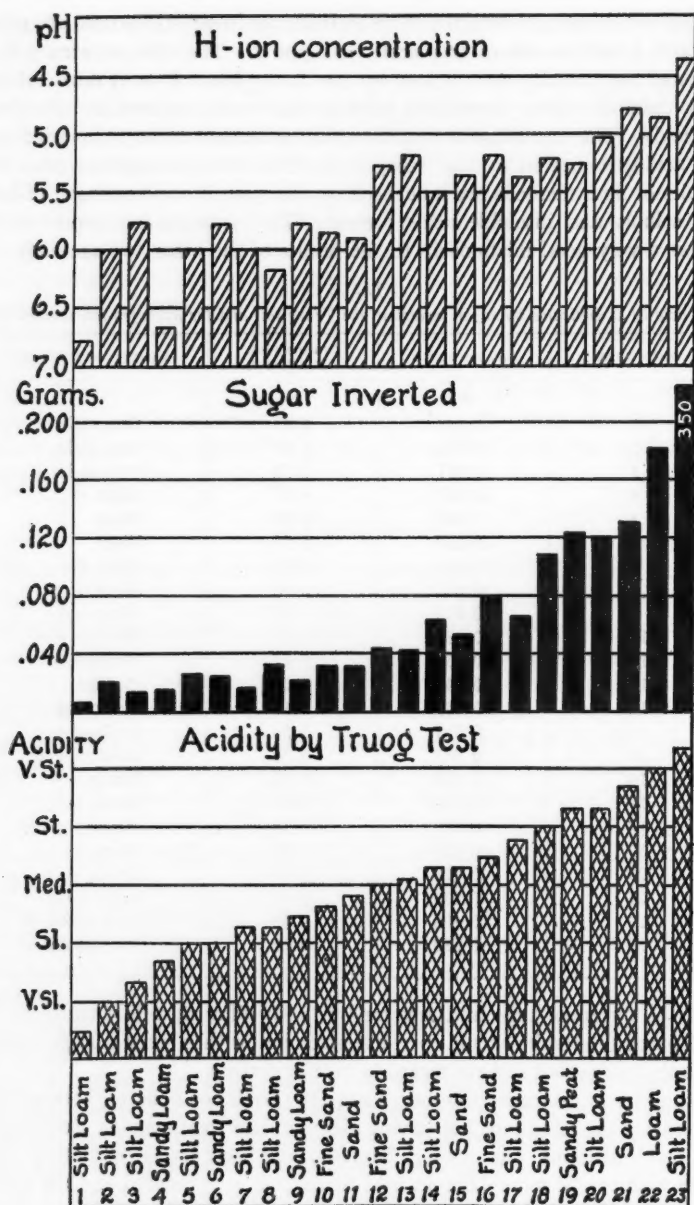
FIG. 1. COMPARISON OF RESULTS OBTAINED ON 23 DIFFERENT SOILS WITH SOIL ACIDITY METHODS INDICATED

In every instance, with one exception, the three methods indicate the same differences in the acidity of the soils due to the different treatments. It is difficult to make a quantitative comparison but a careful analysis of the results indicates, as is also evident in figure 1, that the correlation is best between the results of the sugar inversion method and the Truog test.

TABLE 2

Soil acidity as indicated by sugar inversion, the Truog test and the hydrogen-ion concentration

SOIL	TREATMENT	SUGAR INVERTED	REACTION BY TRUOG TEST	HYDROGEN-ION CONCENTRATION
		gm.		pH
Sand...............	Virgin	0.017	Slight +	5.79
	Cropped	0.026	Medium	5.50
Sandy loam...........	Virgin	Trace	Very slight −	7.53
	Cropped	0.000	Not acid	8.09
Sandy loam...........	Virgin	0.040	Medium +	5.60
	Cropped	0.010	Slight	6.42
Silt loam.............	Virgin	0.024	Medium	5.62
	Cropped	0.021	Slight +	5.88
Silt loam.............	Virgin	0.018	Slight	5.61
	Cropped	0.008	Very slight	6.48
Sand...............	No lime	0.022	Slight	5.50
	Limed	0.000	Very slight −	6.90
Sand...............	Virgin	0.018	Slight +	6.42
	Cropped	0.031	Medium +	5.92
	Limed	Trace	Very slight	6.67
Silt loam.............	Virgin	0.092	Very strong	5.22
	Cropped	0.064	Strong	5.18
	Limed	0.024	Medium	6.00
	Lime and manure	0.014	Slight +	6.06

DISCUSSION

All of the results reported in tables 1 and 2 indicate that there is a very close relation between the degree of acidity indicated by the Truog test and the amount of sugar inverted. When the acidity is low the Truog test is probably nearly as sensitive to small differences in acidity as is the sugar inversion method. When the acidity is high it is difficult to recognize small differences in the intense color produced with the Truog test, and in such cases the sugar inversion method is better for showing differences. Doubtless the Truog test could be readily modified, by using less chemicals, to show greater differences with strongly acid soils.
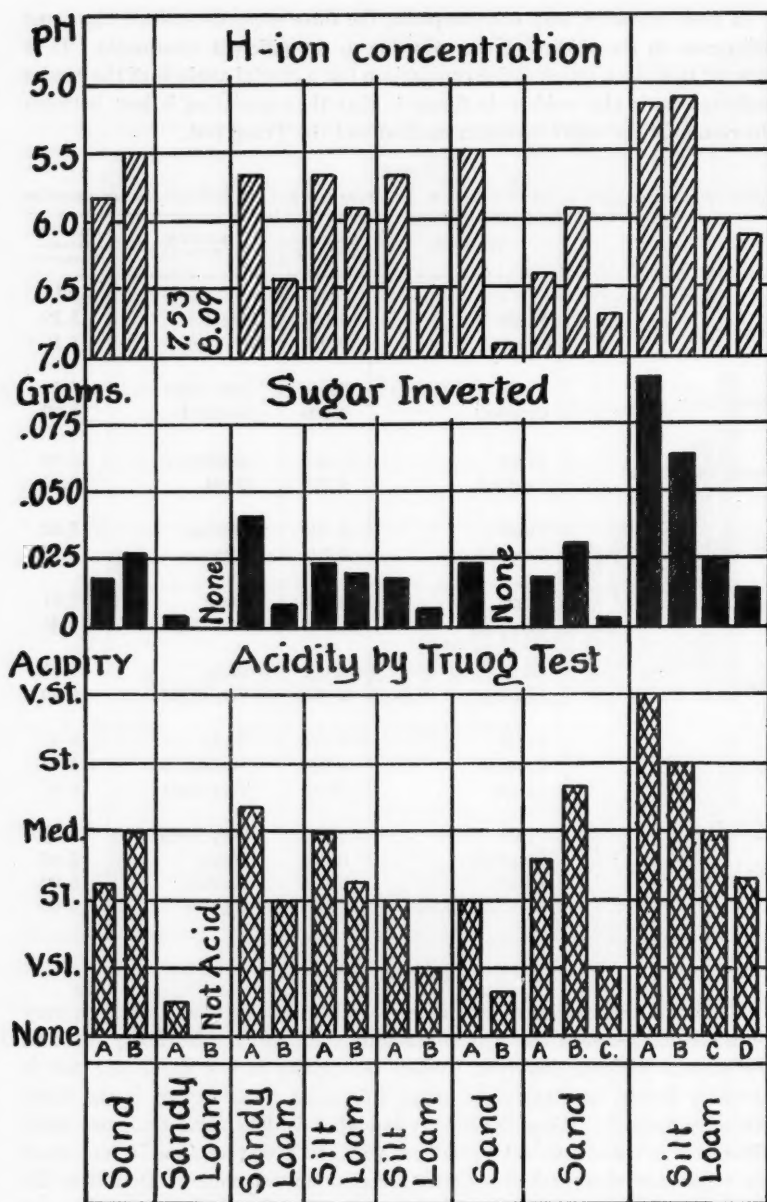
FIG. 2. COMPARISON OF RESULTS OBTAINED ON 8 SOILS VARIOUSLY TREATED WITH SOIL ACIDITY METHODS INDICATED

In general the correlation between the degree of acidity indicated by the Truog test and the hydrogen-ion concentration is good. The reason it is not better given by Truog (8) and Johnson (3) is that the Truog test is a measure of the amount of acids in the soil as well as their avidity.

There is a good general correlation between the amount of sugar inverted and the hydrogen-ion concentration of the soil. This relationship is just as close as that existing between the hydrogen-ion concentration and the results of the Truog test. These results do not agree with those reported by Rice and Osugi (7) for they failed to find any correlation between sugar inversion and the hydrogen-ion concentration. The correlation shown in figures 1 and 2 would doubtless have been better if the hydrogen-ion was the only catalyzer of sugar inversion.

The work of Rice and Osugi and similar experiments performed in this laboratory prove conclusively that the greater part of the inverting action of soil suspensions is due to the presence of the solid phase. For instance, they found that a soil suspension inverted 0.098 gm. of cane sugar while an extract of the same soil inverted only 0.002 gm. Osugi (4) states that the hydrogen-ion concentration of the soil solution is not sufficient to account for the inverting action of soils without assuming a higher concentration of hydrogen-ions about the soil particles than in the mass of the soil solution. He considers acid aluminum silicates to be the cause of the inversion.

In order to determine whether the inverting power of acid soils is due to acid silicates or to a higher concentration of hydrogen-ions around the particles than in the mass of the soil solution, additional experiments were made.

The hydrolysis of ethyl acetate as well as the inversion of cane sugar is catalyzed by hydrogen-ions. So far as is known to the authors, hydrogen-ions are the only catalysts of the hydrolysis of ethyl acetate. Conner (2) has used the hydrolysis of ethyl acetate as a means of determining soil acidity. If in a study of this method the results were found to be similar to those secured with the sugar inversion method, one could only conclude that the same catalyst was influencing both reactions. No information would be obtained as to whether this catalyst consisted of acid silicates or a high concentration of hydrogen-ions ari̇ound the soil particles. However, if the results secured by the two methods differed considerably, one could conclude that different catalysts influenced the reactions or that some catalyst was influencing one reaction and not the other.

Rice and Osugi (7) have offered the following experimental results to prove that the inversion is largely due to the presence of the soil particles. (a) A suspension of acid soil inverts several times as much sugar as an extract of the same soil. (b) Inversion is greater when a soil is kept in suspension by continual shaking than when it is permitted to settle out in the flask. These results have been confirmed by the authors. Similar experiments were then made studying the hydrolysis of ethyl acetate. Soils 5, 12, 17, 20 and 22 of table 1 were used in these experiments. Using a 5-per-cent ethyl acetate

solution the amount of hydrolysis was determined in a water extract, in a soil suspension with continual shaking and in a soil suspension without shaking. The ratio of soil to water in the suspensions was 1:10. For the extract a ratio of 1:2 was used. After hydrolysis had been allowed to go on for 50 hours at room temperature, 50 cc. of the filtered extract was titrated with 0.05 N NaOH. The results are given in table 3.

These results are the reverse of those secured with the sugar inversion method. Hydrolysis was apparently greatest in the water extract and least in the soil suspension that was continually shaken. The low results secured with the soil suspensions may have been due partly to the neutralization of the acetic acid, by acting on minerals of the soil. It is, however, not probable that this would account for all the difference in the order of results

TABLE 3

The hydrogen-ion concentration, sugar inverted and NaOH required to neutralize acidity, developed by the hydrolysis of ethyl acetate in soil suspensions

SOIL	HYDROGEN-ION CONCENTRATION	SUGAR INVERTED	0.05 N NaOH TO NEUTRALIZE ACID IN 100 CC.		
			1:2 Extract	Suspension (shaken)	Suspension (not shaken)
	pH	gm.	cc.	cc.	cc.
Silt loam.....................	6.00	0.025	3.40	0.90	1.80
Fine sand....................	5.23	0.045	5.50	4.50	5.60
Silt loam....................	5.30	0.064	5.40	3.30	3.60
Silt loam....................	5.06	0.120	6.30	3.80	4.40
Loam........................	4.85	0.186	5.10	4.50	5.80

secured by this method and the sugar inversion method. From the results secured it is evident that the high inverting power of a soil suspension as compared to a water extract is not due to a higher concentration of the hydrogen-ions around the soil particles than in the soil solution. If that were the case the two methods would have given similar results since both reactions are catalyzed by hydrogen-ions. The results are readily explained as follows: Both reactions are catalyzed by hydrogen-ions but sugar inversion is also catalyzed by acid silicates which cause most of the inversion in soil suspensions.

Additional studies are being made of the ethyl acetate method but the early results here reported indicate that the concentration of hydrogen-ions around the soil particles is not greater than in the mass of the soil solution. The results also indicate that the hydrolysis of ethyl acetate is not catalyzed by acid silicates as is the inversion of cane sugar.

SUMMARY

1. The results secured by the hydrogen-ion determination, the sugar inversion method, and the Truog soil acidity test were compared on forty-two soils.

2. There was a fairly good correlation between the results of the three methods. The Truog test and the sugar inversion method correlate very well with each other and in a general way both correlate fairly well with the hydrogen-ion concentration.

3. Acid silicates catalyze the inversion of cane sugar and cause the greater part of the sugar inversion in suspensions of acid soils.

4. Acid silicates do not catalyze the hydrolysis of ethyl acetate in soil suspensions.

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STUDIES ON THE TOXIC PROPERTIES OF SOILS[1]

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Since Wheeler and his associates carried out their extensive investigations at the Rhode Island Station on so-called acid soils, students of soil fertility problems have become more or less familiar with the bad effects produced on the soil when sulfate of ammonia is used continuously for a period of years without the addition of lime. It has become customary to say that this practice results in an acid soil, which is more or less toxic to most farm crops.

The long continued use of ammonium sulfate on Hagerstown loam at Pennsylvania State College and on Sassafras loam at this station has given rise to soils quite different in chemical and physical properties from the original soils.

During the past 25 years much has been written about acid soils and many causes of this unfavorable condition have been suggested, but with all that has been said and done there is not yet unanimity of opinion as to the cause of acidity, nor as to the identity of the substance or substances which produce the toxic effects.

Mineral and organic acids, acid salts, soluble aluminum compounds, the removal of basic materials by crops and by drainage waters have been suggested as causes of unproductive acid soils.

Recently considerable attention has been given to soluble aluminum salts as a possible cause of much of the trouble heretofore attributed to "acidity." Those who have followed this phase of the subject at all are already familiar with the work of Abbott (1), Connor (2), Hartwell (4), Denison (3), Mirasol (6), Miyake (7), Ruprecht (9), and others.

Without going into a complete bibliography of the subject, these references will serve to indicate something of the work that has already been done.

In our field work at this station on the availability of different nitrogenous materials, ammonium sulfate is used without lime on Plot 11A and with lime on Plot 11B. The results of the first 10 years have been published and may be referred to for the details of the experiment (5).

Now after 15 years of this treatment the soil on 11A has become so "acid" or toxic as to entirely inhibit the growth of ordinary farm crops. It does how-

ever support a fair covering of sour grass (*rumex acetosella*) during the early summer and later a good covering of crab grass (*digitaria sanguinalis*). Plate 1 illustrates these conditions. The difference in treatment has likewise resulted in distinct physical differences in the two soils. The soil from 11A has a greater water-holding capacity, is closer and finer textured and when made into briquettes has a greater breaking strength than soil from 11B.

Suspecting that the trouble in this case might be due in part to soluble salts of aluminum, it was decided to make a study of the soil from both the limed and the unlimed plots, with a view to clearing up this point. Representative samples were collected from the two plots in the fall of 1921 and after being prepared in the usual way the determinations shown in table 1 were made.

TABLE 1

Analysis of soil from limed and unlimed plots receiving ammonium sulfate

	PLOT 11A	PLOT 11B
Lime requirement (Veitch method).....................................	2,400 pounds CaO per acre	400 pounds CaO per acre
pH values...	4.7	6.4
	per cent	*per cent*
Water-holding capacity.............................	38.700	30.1
Total nitrogen.......................................	0.093	0.074
Total P_2O_5.......................................	0.111	0.112
Total carbon..	1.250	1.110
Total Al_2O_3, Fe_2O_3 and P_2O_5 by H_2SO_4	6.440	4.140
Fe_2O_3..	1.860	1.210
Al_2O_3 (by difference)...............................	4.460	2.820
Total SO_3..	0.058	0.017

These figures reveal certain differences which may have a more or less important bearing on the problem. There is a pronounced difference in soil reaction, the soil from 11A showing a pH value of 4.7 and that from 11B a pH value of 6.4. By the Veitch method 11A shows a lime requirement of approximately $2\frac{1}{4}$ tons per acre, while 11B is near the neutral point. It is significant that the water-holding capacity, total nitrogen and total carbon are all higher for 11A than for 11B. This would seem to indicate a more rapid disappearance of organic matter from the limed than from the unlimed plot. There is likewise a higher percentage of iron and aluminum in soil from 11A than in that from 11B. There may be some significance in the higher percentage of sulfur in 11A than 11B. Further reference will be made to this.

WATER-SOLUBLE IRON AND ALUMINUM COMPOUNDS

Following out the suggestion that soluble aluminum compounds might be partly responsible for the toxic condition of the soil on plot 11A, 5 kgm. of the dry soil were placed in a lysimeter made by inverting a bell glass having

FIG. 1. UNLIMED SULFATE OF AMMONIA PLOT
Sour grass and crab grass come in where timothy should grow

FIG. 2. LIMED SULFATE OF AMMONIA PLOT
A good crop of timothy

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PLATE 2

FIG. 1. CULTURE-SOLUTION, SERIES 1

1. Extract from 11A.
2. Extract from 11A + 0.2 gm. $NaNO_3$.
3. Extract from 11B.
4. Extract from 11B + 0.2 gm. $NaNO_3$.
5. Extract from 11A + lime water.
6. Extract from 11A + 0.5 gm. KH_2PO_4.
7. Extract from 11B + 0.5 gm. KH_2PO_4.
8. Control solution.

FIG. 2. CULTURE-SOLUTION, SERIES 2

1. Control solution.
2. Extract from 11A.
3. Extract from 11B.
4. Extract from 11A + lime water, pH 6.9.
5. Extract from 11A + lime water, pH 8.4.
6. Extract from 11A + NH_4OH.
9. Extract from sulfur plot 5, limed.
10. Extract from sulfur plot 10, unlimed.
11. Extract from sulfur plot 10 + lime water.
12. Extract from sulfur plot 10 + acid phosphate.

FIG. 3. CULTURE-SOLUTION, SERIES 3

1. Control solution.
2. Extract from plot N, unlimed.
3. Extract from plot N + $CaH_4 (PO_4)_2$.
4. Extract from plot N + lime water.
5. Extract from plot N + NH_4OH treatment.
6. Extract from plot N + $NH_4H_2PO_4$.
7. Extract from plot N + KH_2PO_4.
8. Extract from plot M, limed.
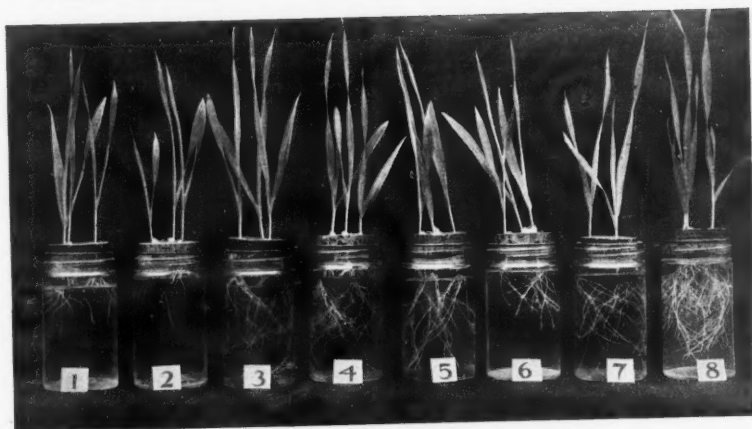
FIG. 1
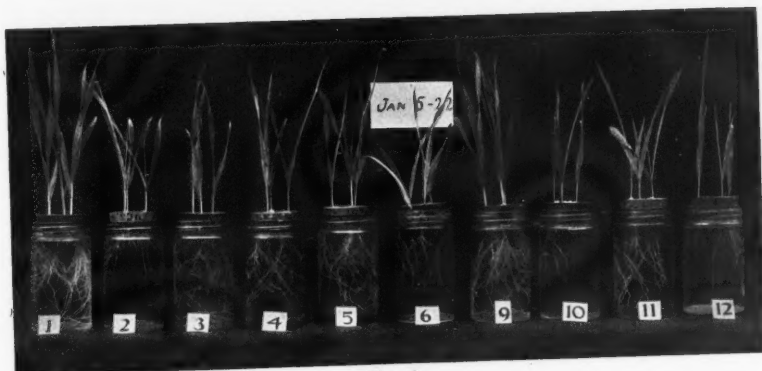
FIG. 2

FIG. 3

PLATE 3

Fig. 1. Culture-Solution, Series 3, Continued

1. Control solution.
9. Extract from plot 11A, unlimed.
10. Extract from plot 11A + CaH$_4$(PO$_4$)$_2$.
11. Extract from plot 11A + NH$_4$OH treatment.
12. Extract from plot 11A + NH$_4$H$_2$PO$_4$.
13. Extract from plot 11A + KH$_2$PO$_4$.
14. Extract from plot 11A 2nd liter leachings.
15. Extract from plot 11A 3rd liter leachings.
16. Extract from plot 11A + 50 cc. control solution.
20. Extract from plot 11B, limed.

Fig. 2. Culture-Solution, Series 4

1. Control solution.
2. Extract from plot 11A, the solution used for culture 9, plate 3 fig. 1, + ammonia treatment.
3. Extract from plot 11A, the solution used for culture 10, plate 3 fig. 1 + ammonia treatment.
4. Extract from plot 11A and ammonia treatment + Fe.
5. Extract from plot 11A and ammonia treatment + Fe and P$_2$O$_5$.
6. Extract from plot 11A with ammonia treatment.
7. Extract from plot 11A evaporated to dryness and ignited.
8. Extract from plot 11B treated as in No. 7.
9. Extract from plot 11A unlimed.

Fig. 3. Culture-Solution, Series 4, Continued

1. Control solution.
9. Extract from plot 11A, unlimed.
10. Like No. 5 (Fig. 2) + 0.01 gm. aluminum sulfate.
11. Like No. 5 (Fig. 2) + 0.025 gm. aluminum sulfate.
12. Like No. 5 (Fig. 2) + 0.05 gm. aluminum sulfate.
13. Like No. 5 (Fig. 2) + 0.10 gm. aluminum sulfate.
14. Like No. 5 (Fig. 2) + 0.20 gm. aluminum sulfate.
20. Extract from plot 11B, limed.
21. Like No. 5 (Fig. 2) + H$_2$SO$_4$ to pH 4.6.
22. Like No. 5 (Fig. 2) + H$_2$SO$_4$ to pH 4.2.
23. Like No. 5 (Fig. 2) + H$_2$SO$_4$ to pH 3.5.

PLATE 3

TOXIC PROPERTIES OF SOILS
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FIG. 1

FIG. 2

FIG. 3

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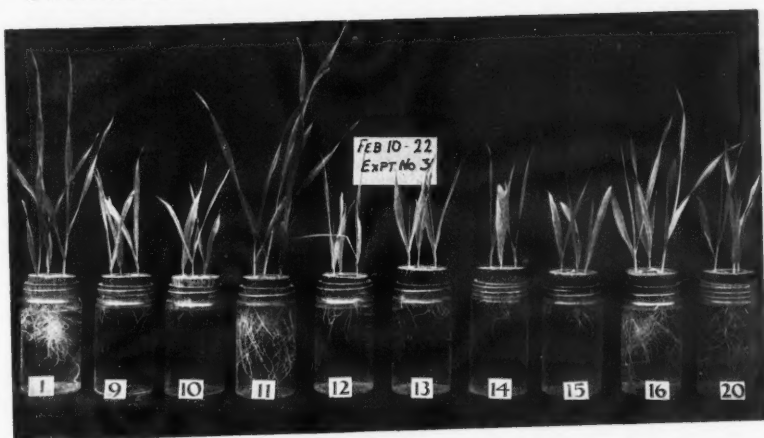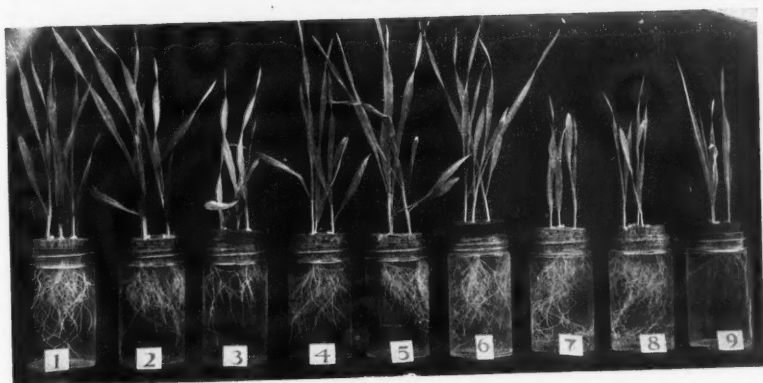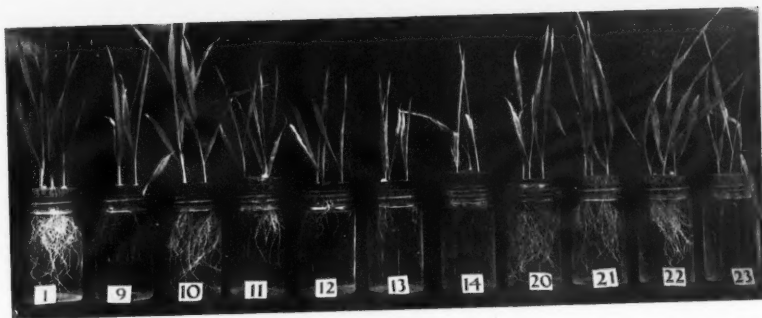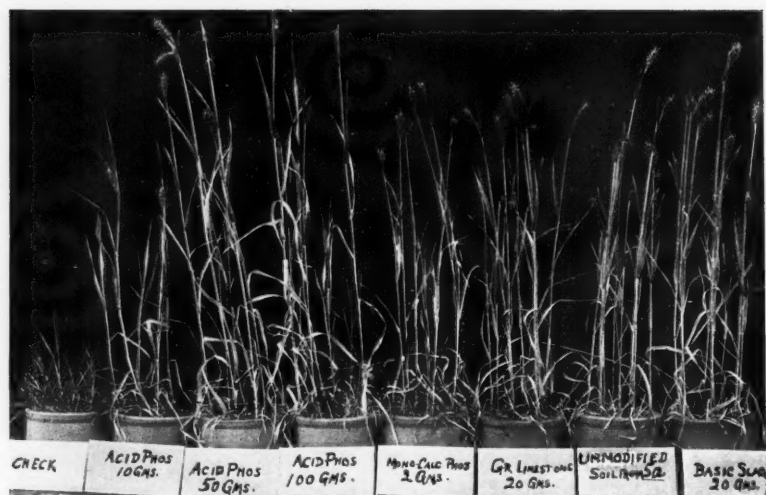
FIG. 1. POT EXPERIMENT, SERIES 2
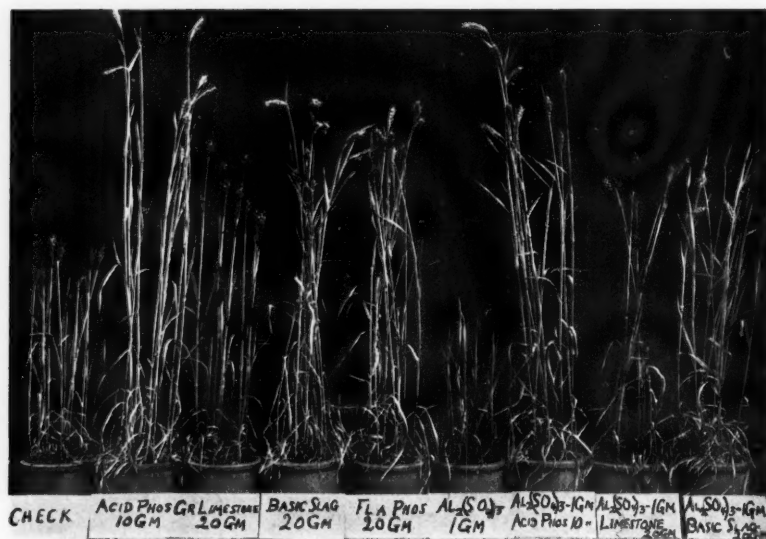
FIG. 2. POT EXPERIMENT, SERIES 3

an opening at the top, and percolating distilled water through the mass of soil until the leachings amounted to one liter. The extract thus obtained was used for determining the soluble aluminum and other constituents, and also as a culture medium for growing plants. A similar extract was obtained from 11B for comparison. The analytical results for the two plots are reported in table 2.

From these figures it will be observed that the first liter of extract from 11A yielded 32.2 mgm. of combined iron and aluminum oxides, the greater part of which is alumina, whereas the liter of extract from 11B yielded only a trace of the combined oxides. The second liter from 11A yielded 9 mgm. and the third 7.5 mgm. Thus the three liters of extract yielded soluble iron and aluminum compounds equivalent to nearly 50 mgm. of the combined oxides,

TABLE 2

Analysis of a 1-liter water-extract from 5 kgm. dry soil

MINERALS	PLOT 11A	PLOT 11B
	mgm.	*mgm.*
$Fe_2O_3 \cdot Al_2O_3$	32.2	Trace
Fe_2O_3	4.0	.....
Al_2O_3	28.2	.....
CaO	95.5	70.80
P_2O_5	1.97	4.77
$Fe_2O_3 \cdot Al_2O_3$		
(2nd liter of leachings)	9.00	.....
(3rd liter of leachings)	7.50	.....

nearly all of which was alumina. In this connection it may be pointed out that 11A furnished less than half as much water-soluble phosphoric acid as 11B. This may be due to the presence of the large amount of soluble aluminum compounds in the soil from 11A, which would tend to render the phosphoric acid insoluble.

Although the lime requirement for 11B is much less than for 11A, the liter of extract from the latter yielded 95.5 mgm. of lime (CaO), whereas an equal amount of extract from 11B yielded only 70.8 mgm. of CaO. This seeming contradiction may be the result of the action of the sulfuric acid radical on the calcium of the soil silicates with the formation of calcium sulfate, which on account of the physical condition of the soil may not be leached out as rapidly as it is from 11B. The higher percentage of SO_3 found in 11A would seem to lend support to this view.

However this may be, it is certain that the lime which has been applied to 11B has rendered the aluminum less soluble on this plot than it is on 11A.

CULTURE-SOLUTION WORK

Culture solution series 1

As already noted, culture-solution work was carried out with the extract prepared by treating 5 kgm. of the soil with sufficient distilled water to obtain 1 liter. This extract was used without modification, as a culture medium for growing barley plants and also with certain modifications as hereafter indicated. An extract made in the same way from the soil of 11B was used for comparison. Table 3 shows the treatments together with the pH values of the solutions at the beginning and at the end of the experiment, and the relative weights of the crops, when dried.

TABLE 3

Series 1; Modified soil extract as a culture solution—reaction of solution and relative weights of crop

CULTURE NUMBER		REACTION		RELATIVE WEIGHTS	
		Initial	Final	Tops	Roots
		pH	pH		
	Extracts from:				
1	Plot 11A..	4.7	4.7	82.8	68.2
2	Plot 11A + 0.2 gm. NaNO₃.....................	4.7	4.8	64.2	56.8
3	Plot 11B..	6.8	6.4	77.7	114.1
4	Plot 11B + 0.2 gm. NaNO₃.....................	6.9	7.1	64.9	75.0
5	Plot 11A + 13.5 cc. lime water.................	6.8	6.8	71.1	83.8
6	Plot 11A + 0.5 gm. KH₂PO₄.....................	3.8	4.2	65.7	70.0
7	Plot 11B + 0.5 gm. KH₂PO₄.....................	5.4	5.5	63.8	106.9
8	Shive's 3 salt nutrient solution (R₅C₂).............	4.6	4.7	100.0	100.0

The weights of the plants grown in a 3-salt nutrient solution (Shive's R_5C_2)[2] were taken as 100 and the actual weights for the various treatments have been converted on this basis.

Plates 2 and 3 show the method of growing the plants, and also give a clear idea of the top and root growth in each case. The seedlings were grown for a period of about two weeks. Table 3 brings out a number of points of specific interest. It is especially significant that the 3-salt solution used as a check had in the beginning essentially the same pH value as the extract from 11A, but the latter (culture 1) gave a much poorer root growth than the check. The extract from 11B (culture 3), the soil of which has received the same ammonium sulfate treatment as 11A, but which has been limed at intervals of 5 years, had at the beginning, a pH value of 6.8 and gave a root growth of 114 as compared with 100 for the check. Again the extract from 11B plus

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[2] 36 cc. KH₂PO₄ M/2 ⎫
   10 cc. Ca(NO₃)₂ M/2 ⎬ Made to 1 liter (1.75 atmospheres).
   30 cc. MgSO₄ M/2 ⎭

½ gm. of acid potassium phosphate (culture 7), with a pH value of 5.4, gave a root growth of 106.9, on the scale of 100 for the check, which is almost as much as the yield with the extract from 11B, unmodified, having a pH value of 6.8.

Extract 11A plus 13.5 cc. of lime water (culture 5) with a pH value of 6.8 (almost at the neutral point) gave a relative root growth of 83.8, which is distinctly less than the growth on culture 7 although the latter is decidedly more acid than the former. Nitrate of soda added to the extract depressed rather than increased plant growth.

These results would seem to indicate that acidity is not the only factor which has tended to hinder growth in this case.

Culture-solution series 2

The second series of culture solutions which was set up included extract from 11A and 11B and also from two heavily sulfured plots, one of which had subsequently been limed. Table 4 and plate 2 figure 2 show the arrangement and results.

TABLE 4

Series 2; Modified soil extract as a culture solution—reaction of solution and relative weights of crop

CULTURE NUMBER		REACTION		RELATIVE WEIGHTS	
		Initial	Final	Tops	Roots
		pH	*pH*		
1	Shive's 3 salt solution (R₅C₂).....................	4.6	5.4	100.0	100.0
	Extract from:				
2	Plot 11A....................................	4.5	4.5	41.2	73.8
3	Plot 11B....................................	7.2	7.0	36.1	112.5
4	Plot 11A + lime water.......................	6.9	6.6	42.1	82.6
5	Plot 11A + lime water.......................	8.4	7.0	43.7	98.8
6	Plot 11A + NH₄OH and filtered to remove Fe and Al...	6.7	5.0	42.3	43.1
7*	Plot 11A + 2½ gm. acid phoshate..............	3.4	....	....	....
8*	Plot 11A + 5 gm. acid phosphate..............	3.2	....	....	....
9	Sulfur plot 5 limed..........................	6.8	7.2	69.9	115.8
10	Sulfur plot 10 unlimed.......................	4.6	4.6	30.4	59.6
11	Sulfur plot 10 + lime water..................	6.8	6.3	29.6	58.6
12	Sulfur plot 10 + 5 gm. acid phosphate..........	3.4	3.6	32.1	26.3

* Plants in these cultures were a failure.

Here it will be noted that the 3-salt solution gave an excellent top and root growth notwithstanding the fact that the pH value was almost as low as that of extract 11A. Also extract 11B (culture 3) and extract 11A plus lime water (cultures 4 and 5), and sulfur plot 5 (culture 9) have all given excellent root growth.

Very poor root growth was secured with extract 11A (culture 2), sulfur plot 10 (culture 10) and sulfur plot 10 plus 5 gm. of acid phosphate (culture 12). In this last case the failure was no doubt as much due to the low pH value as to any other cause. In the case of culture 6 where ammonium hydroxide was added to extract 11A, it is quite possible the results would have been different if the solution had been boiled before it was filtered. Later work causes us to suspect that in this case we failed to remove all of the soluble aluminum salts, or that there was an excess of free ammonia.

The influence of the lime water in cultures 4 and 5 is noteworthy. This leads us to suggest that the calcium ion has a balancing effect on the aluminum even though the latter may not all be removed from the solution.

Culture-solution series 3

A third series was set up in which extracts from plots 11A and 11B were used in comparison with extracts from plots M (limed) and N (unlimed). For a number of years acid phosphate and muriate of potash have been used on plots M and N, but no ammonium sulfate or sulfur has been applied. No lime has been applied to plot N for a period of 15 years or longer, while plot M is limed at intervals of 5 years. These plots have been planted to soybeans continuously for a period of 10 years. Plot M produces each year an excellent crop while plot N has recently fallen to a yield of only a little more than a bushel per acre.

The arrangement of the series is indicated in table 5 and also plate 2, figure 3 and plate 3 figure 1.

In connection with this table it will be observed that extracts N and 11A (cultures 2 and 9) both gave a very low yield of tops and roots, but when these extracts were boiled with ammonium hydroxide and the precipitate removed and a small amount of iron and phosphoric acid added (cultures 5 and 11), each gave a total growth of roots and tops equal to or exceeding the growth made by the standard culture solution, notwithstanding the fact that the pH values were 5.2 and 5.1 respectively at the beginning and 4.6 and 4.0 respectively at the end. The yield of tops and roots, it will be noted, was about the same as the yield with the extract from plot M which began with a pH value of 7.0. It is thus quite clear that the ammonium hydroxide treatment puts out of action something that the mono-calcium phosphate (cultures 3 and 10) cannot counteract.

The response to the ammonium hydroxide treatment can hardly be attributed to the nitrogen, since nitrate of soda added to extract 11A in series 1 gave a lower yield than the unmodified extract, that is to say, nitrogen does not appear to be a limiting factor in the extract.

Potassium acid phosphate (cultures 7 and 13) lowered the pH value, but increased the yield over the untreated extracts in each case.

Ammonium acid phosphate lowered the pH value of both extracts, and in the case of plot N (culture 6) increased the yield over the untreated extract from this plot.

Cultures 14 and 15 constituting the second and third liter of leachings, respectively, from 11A, showed no root development and very poor tops. Culture 16 which represented the third liter of leachings from 11A and which was reinforced with 50 cc. of the 3-salt control solution gave very good root and top growth, though the weights of these are not reported in the table. It is possible that in this case the 50 cc. of control solution carried sufficient basic materials to counteract the toxic effect of the 11A extract.

TABLE 5

Series 3; Modified soil extract as a culture-solution—reaction of solution and relative weights of crop

CULTURE NUMBER		REACTION		RELATIVE WEIGHTS	
		Initial	Final	Tops	Roots
		pH	pH		
1	Shive's 3 salt solution (R_6C_2)......................	4.6	5.6	100.0	100.0
	Extracts from:				
2	Plot N..	4.8	6.6	29.1	36.2
3	Plot N + 0.1 gm. $CaH_4 (PO_4)_2$..................	4.0	4.8	31.0	55.8
4	Plot N + lime water...........................	7.0	6.6	25.5	50.1
5	Plot N + NH_4OH, boiled and filtered, + small amount of Fe and P_2O_5........................	5.2	4.6	72.8	114.2
6	Plot N + 0.1 gm. $NH_4H_2PO_4$..................	4.4	4.4	36.4	49.8
7	Plot N + 0.1 gm. KH_2PO_4.....................	4.6	5.0	31.5	48.4
8	Plot M..	7.0	6.9	73.0	122.6
9	Plot 11A......................................	4.6	4.6	31.0	46.2
10	Plot 11A + 0.1 gm. $CaH_4(PO_4)_2$..............	3.4	4.2	26.0	52.4
11	Plot 11A + NH_4OH, boiled and filtered, + small amount Fe and P_2O_5.........................	5.1	4.0	126.6	88.3
12	Plot 11A + 0.1 gm. $NH_4H_2PO_4$................	3.7	4.4	25.0	35.5
13	Plot 11A + 0.1 gm. KH_2PO_4..................	3.8	4.4	32.7	42.3
14	Plot 11A, 2nd liter of leachings..................	4.6	4.4	....	....
15	Plot 11A, 3rd liter of leachings..................	4.6	3.8	....	....
16	Plot 11A + 50 cc. Standard 3-salt solution.......	4.6	5.6	....	....
20	Plot 11B......................................	7.2	6.4	41.1	120.0

It should be stated here that a liter of extract from plot N prepared as in the case of 11A yielded soluble iron and aluminum salts to the amount of 12 mgm. of $Al_2O_3 \cdot Fe_2O_3$, of which only a trace was iron. Plot M yielded no soluble iron and aluminum.

Culture-solution series 4

The fourth culture-solution was set up to further study the effect of modifying the extract from 11A. Barley was grown in this as in the previous series. The results are shown in table 6 and in plate 3, figures 2 and 3.

Here, as in the other series, the weights with the 3-salt solution were taken as 100 and the other weights calculated on this basis. An examination of the

table shows that cultures 2, 4, 5 and 6, all of which were the extract from 11A treated with ammonia to remove the aluminum compounds, gave very fair yields of both roots and tops. This is well shown in figure 2. In this connection it may be pointed out that in only one out of these four cultures was the pH value as high as 6.8 at the beginning, and that it was lower in all four at the end of the experiment than at the beginning.

TABLE 6

Series 4; Modified soil extract as a culture solution—reaction of solution and relative weights of crop

CULTURE NUMBER		REACTION		RELATIVE WEIGHTS	
		Initial	Final	Tops	Roots
		pH	pH		
1	Shive's 3 salt solution (R_5C_2)......................	4.6	5.2	100.0	100.0
	Extract from:				
2	Plot 11A (same as used in series 3) but treated with ammonia to remove Al and Fe................	4.8	3.7	73.2	48.9
3	Plot 11A + 0.1 gm. $CaH_4(PO_4)_2$ (same as used in No. 10 series 3) but treated with ammonia to remove Al and Fe............................	5.0	4.7	36.2	25.5
4	Plot 11A with ammonia treatment to remove Al and Fe and a small amount of Fe added............	6.6	4.8	63.2	47.3
5	Plot 11A with ammonia treatment and a small amount of Fe and P_2O_5 added.................	5.0	3.9	70.6	36.4
6	Plot 11A with ammonia treatment...............	6.8	4.8	50.7	46.7
7	Plot 11A, evaporated to dryness, ignited and residue made to 200 cc. with distilled water.............	7.2	6.0	24.5	63.2
8	Plot 11B treated as in No. 7.....................	7.8	6.7	22.0	47.6
9	Plot 11A unmodified............................	4.6	4.6	34.5	30.5
10	Same as No. 5 + 0.01 gm. $Al_2(SO_4)_3 \cdot 18H_2O$........	4.6	4.3	62.5	46.6
11	Same as No. 5 + 0.025 gm. $Al_2(SO_4)_3 \cdot 18H_2O$.......	4.2	4.4	30.4	29.4
12	Same as No. 5 + 0.050 gm. $Al_2(SO_4)_3 \cdot 18H_2O$.......	3.5	3.8	20.2	31.7
13	Same as No. 5 + 0.100 gm. $Al_2(SO_4)_3 \cdot 18H_2O$.......	3.3	3.6	15.6	23.7
14	Same as No. 5 + 0.200 gm. $Al_2(SO_4)_3 \cdot 18H_2O$.......	3.1	3.4	18.4	20.5
20	Plot 11B unmodified............................	6.8	6.4	28.5	51.8
21	Same as No. 5 + H_2SO_4 to make reaction pH 4.6....	4.6	3.8	65.6	29.7
22	Same as No. 5 + H_2SO_4 to make reaction pH 4.2....	4.2	4.0	48.9	36.8
23	Same as No. 5 + H_2SO_4 to make reaction pH 3.5....	3.5	3.9	27.1	36.5

This lowering of the pH value in the presence of ammonium salts is in accord with recent work reported by Prince, Jones and Shive (8). They analyzed culture-solutions and concluded that the lowering of the pH values, when ammonium salts were present, was due, in all probability, to a difference in ion absorption by the plants, i.e., there was greater absorption of the ammonia ion than of the acid ion. Furthermore, in the absence of ammonium salts the reaction change in nutrient solutions in contact with the roots of

growing plants was towards the neutral point when a considerable amount of $Ca(NO_3)_2$ was present. Prince, Jones and Shive (8) found that this change was directly correlated with high nitrate absorption. This idea is borne out by the reaction change of the standard culture solution, tables 4, 5 and 6.

In the case of culture 7, 200 cc. of the 11A extract was evaporated to dryness, ignited and the residue taken up with distilled water and used as a culture medium in the same way that the original extract was used. This, it will be observed, gave a very good root growth, though the plants were small.

The unmodified extract from 11A gave very poor root growth, the short stubby character of which is shown in culture 9.

Culture 10 with 0.01 gm. aluminum sulfate contained 1.53 mgm. Al_2O_3, whereas culture 9 contained by analysis 5.64 mgm. Al_2O_3. Comparing this with cultures 4 and 5 where 11A was treated with ammonia, it would appear that the small amount of alumina contained in culture 10 was not harmful to the plants, but when larger amounts were added, cultures 11–14 inclusive, the yield was reduced to less than the yield from the unmodified solution of 11A (culture 9). Since the increase in the amount of aluminum sulfate resulted in the lowering of the pH values, the injury may possibly be attributed partly to increased acidity and partly to increase in the amount of soluble aluminum.

Culture 10, which received the ammonia treatment (same as culture 5) with the addition of 0.01 gm. aluminum sulfate, gave a good growth of both roots and tops, but as the amount of aluminum sulfate was increased (cultures 11–14) the root and top growth was gradually depressed, the roots having the short stubby appearance observed in the unmodified extract from 11A. The pH value likewise decreased as the amount of aluminum sulfate was increased. It is significant that the results with 0.025 gm. and 0.05 gm. aluminum sulfate are quite similar to the results with the unmodified extract from 11A. The extract from 11B gave good results as indicated in culture 20.

Cultures 21, 22 and 23 were prepared by treating 11A extract with ammonia as in culture 5 and then adding dilute sulfuric acid to bring the pH values to 4.6, 4.2 and 3.5 respectively, thus giving pH values corresponding exactly with the pH values of cultures 10, 11 and 12. In the case of the former however, the plants were healthier in appearance than they were in the latter, and the sulfuric-acid treated cultures invariably gave larger yields (roots and tops) than the cultures which received the aluminum sulfate treatment. With the pH value down to 3.5 as in cultures 12 and 23, root development was seriously interfered with.

It is quite apparent from the results of this series that a culture solution may have a pH value as low as 4.6 and still give normal root development if the soluble aluminum has previously been removed by precipitation with ammonia. On the other hand a pH value of about 4.6 or lower with soluble aluminum salts present gives rise to a short stubby root growth, and usually depresses the top growth also.

VEGETATION TESTS WITH ACID SOILS

Series 1

In this experiment barley was grown in glazed earthenware pots holding 3.5 pounds of soil from plot 11A, with special treatments as indicated in table 7.

The treatments were carried out in triplicate but for the purpose of condensing the report only the average for the 3 pots of each treatment is given. It will be remembered that this soil is distinctly acid having a pH value of about 4.6. At the close of the experiment a composite sample was made by sampling each of the 3 pots having the same treatment, and pH determinations were again made. These are reported in the table along with the dry weights of the crop.

TABLE 7

Series 1; Modified soil cultures—yield of dry matter and reaction of soil

POT NUMBER	SPECIAL TREATMENT	DRY MATTER	FINAL REACTION
		gm.	pH
1	Nothing...	0.0	4.7
2	10 gm. acid phosphate...............................	5.2	4.5
3	20 gm. acid phosphate...............................	6.3	4.6
4	Distilled water extract of acid phosphate..............	4.1	4.6
5	20 gm. ground limestone.............................	9.0	7.5
6	20 gm. wood ashes..................................	6.1	6.6
7	20 gm. basic slag...................................	9.5	7.25
8	20 gm. Florida phosphate............................	4.4	5.3
9	5 gm. ammonium phosphate..........................	2.8	4.9
10	5 gm. mono-calcium phosphate.......................	5.7	4.7
11	1 gm. nitrate of soda...............................	0.0	4.7
12	Watered with dilute solution calcium nitrate............	0.0	4.7
13	Soil previously leached with distilled water.............	0.0	4.7
14	Soil roasted in furnace...............................	4.1	5.6

The pots with untreated soil produced no barley,—only a small growth of crab grass. The pots that received acid phosphate gave a fair crop of barley but it should be noted that the applications of phosphate were exceedingly heavy, 20 gm. for 3½ pounds of soil being about equivalent to 25,000 pounds per acre. The crop was better with 20 gm. of acid phosphate than with 10 gm. The best yields, however, were obtained with ground limestone and with basic slag, and where these materials were used the pH values rose to 7.5 and 7.25, respectively. Wood ashes gave a yield almost as high as the 20 gm. of acid phosphate and raised the pH value of the soil to 6.6. Ground Florida phosphate rock and mono-calcium phosphate gave smaller yields than the 20-gm. application of acid phosphate. The Florida phosphate raised the pH value nearly 1 point, but the mono-calcium phosphate changed it only slightly.

Plants in the pots that received nitrate of soda and those that were watered with a solution of calcium nitrate were a failure, as were also those grown

in the leached soil. The roasted soil (heated so that organic matter was destroyed) showed an improvement as compared with the untreated soil. The roasting process, it will be observed, raised the pH value from 4.7 to 5.6, and it undoubtedly tended to convert soluble aluminum salts into the less harmful oxides.

These results are quite in accord with the culture solution work in showing that basic materials are most efficient in counteracting toxic substances contained in this soil. Two other series of pots were set up after this plan with soil from 11A, one of which was seeded to buckwheat and the other to rape, but the crops grew very slowly and were not harvested. It was quite evident, however, that had they been harvested and weighed the results would have corresponded in general to the results of the barley.

Series 2

The soil used in this experiment was taken from the plot which had previously received a heavy application of sulfur and which became very acid (pH 4.4 to 4.5) due to the oxidation of the sulfur.

TABLE 8

Series 2; Modified soil cultures—yield of dry matter and reaction of soil

POT NUMBER	SPECIAL TREATMENT	AVERAGE YIELD OF DRY BARLEY	FINAL REACTION
		gm.	pH
1–2	Check (untreated soil)...............................	Nothing	4.4
3–4	1 gm. acid phosphate...............................	Nothing	4.2
5–6	10 gm. acid phosphate..............................	3.15	4.25
7–8	50 gm. acid phosphate..............................	7.70	4.9
9–10	100 gm. acid phosphate.............................	6.25	5.3
11–12	1 gm. Mono-calcium phosphate.....................	2.55	4.4
13–14	2 gm. Mono-calcium phosphate.....................	3.80	4.5
15–16	1 gm. acid potassium phosphate....................	4.30	4.5
17–18	2 gm. acid potassium phosphate....................	4.55	4.5
19–20	20 gm. ground limestone...........................	8.90	7.2
21–22	Untreated soil from *limed, sulfur* plot (5a)..............	7.95	7.4
23–24	20 gm. basic slag..................................	9.25	7.5

As in the other series 3.5 pounds of soil was used and special treatments, in duplicate, were given as indicated in table 8. Ten barley seeds were planted in each pot and the pots were kept at optimum moisture condition by the addition of water at intervals. Table 8 shows the average weights of barley at maturity and the pH value of the soil for the different treatments.

Germination was poor in the untreated soil and also in those soils that received acid phosphate. For the pots with untreated soil and those that received only 1 gm. of acid phosphate the crop was a failure. With 50 and 100 gm. of acid phosphate the crops were fair (see plate 4, fig. 1). The monocalcium and potassium phosphates gave poor yields. Twenty grams of ground

limestone and 20 gm. of basic slag both gave good results, the basic slag show-
ing the highest average as it did in series 1. The untreated soil from the
limed sulfur plot also gave a good yield. This soil had been treated with
sulfur at the same time the other soil was treated but about a year after the
sulfur was applied it had been heavily limed, and at the time this experiment
was started it had a pH value of a little above 7, which was about the same as
the soil of the pots which received lime and basic slag.

It will be noted that in nearly all the other cases the pH value was below 5.
It is significant that with a pH value of 4.9 pots 7 and 8 (table 8) gave an average
yield of 7.7 gm. which is but little less than the yield with basic slag, having
a pH value of 7.5.

Series 3

The soil used in this third series of pots was an acid silt loam which had
been without any lime or fertilizer treatment for many years. As in the pre-
ceding experiment, pots holding 3.5 pounds of soil were used. Special treat-

TABLE 9

Series 3; Modified soil cultures—yield of dry matter and reaction of soil

POT NUMBER		AVERAGE YIELD OF DRY BARLEY	FINAL REACTION
		gm.	pH
1–2	Check (untreated soil)...............................	4.5	5.3
3–4	0.5 gm. $Al_2(SO_4)_3$	3.9	5.4
5–6	1 gm. $Al_2(SO_4)_3$	2.2	5.3
7–8	10 gm. Acid phosphate.............................	12.8	5.0
9–10	20 gm. Ground limestone...........................	7.4	7.6
11–12	20 gm. Basic slag.................................	13.4	7.3
13–14	20 gm. Florida rock phosphate.......................	11.4	6.1
15–16	20 gm. dibasic silicate............................	12.2	8.0
17–18	1 gm. $Al_2(SO_4)_3$ + 10 gm. acid phosphate............	10.9	5.1
19–20	1 gm. $Al_2(SO_4)_3$ + 20 gm. ground limestone..........	9.3	7.6
21–22	1 gm. $Al_2(SO_4)_3$ + 20 gm. basic slag.................	12.6	7.3
23–24	1 gm. $Al_2(SO_4)_3$ + 20 Florida rock phosphate.........	9.95	5.9
25–26	1 gm. $Al_2(SO_4)_3$ + 20 gm. dibasic silicate............	13.7	7.8
27–28	Check (untreated soil)...............................	5.12	5.4
29–30	0.5 gm. $Al(NO_3)_3$...................................	3.00	5.3
31–32	1 gm. $Al(NO_3)_3$....................................	1.60	5.3
33–34	0.5 gm. $Al(NO_3)_3$ + 10 gm. acid phosphate............	13.70	5.0
35–36	0.5 gm. $Al(NO_3)_3$ + 20 gm. ground limestone..........	7.2	7.6

ments were given as indicated in table 9. The work was carried out in dupli-
cate and 10 seeds of beardless barley were planted in each pot.

Germination was about 70 per cent in the untreated soil and 80 to 100 per
cent for the various treatments. The table shows the dry weights of barley
at maturity and the pH values of the soil representing the different treatments.

The yield with the untreated soil was small, and with 1 gm. of aluminum
sulfate it was even less. With 10 gm. of acid phosphate (pots 7 and 8) it was

very much better, although the pH value of this soil, at the end of the experiment, was lower than that of the untreated soil (see plate 4, fig. 2 and table 9).

Additions of ground limestone, basic slag, Florida phosphate rock and dicalcic silicate all resulted in yields well above those obtained with the untreated soil. Also with these treatments the pH values were materially increased, dicalcic silicate raising it to pH 8. When, in addition to the acid phosphate and basic materials mentioned, 1 gm. of aluminum sulfate was applied (pots 17–26 inclusive) the yields were reduced only slightly or not at all as compared with the yields when the acid phosphate and basic materials were used without the aluminum sulfate. With 0.5 gm. and 1 gm. of aluminum nitrate the yields were even lower than when like quantities of aluminum sulfate were used. However with the addition of acid phosphate (pots 33 and 34) and ground limestone (pots 35 and 36) the yields were again raised, the former giving an average of 13.7 gm. and the latter 7.2 gm. It should be noted that in this case the acid phosphate treated soil, with a pH value of 5, gave a much better yield than the limestone treated soil with a pH value of 7.6.

From the data secured with pots 7–8, 17–18, and 33–34 it is quite evident that acidity is not the only factor which is responsible for low yields. These pots, having at the end of the experiment pH values of about 5, gave yields almost as large as any of the pots treated with basic materials and having pH values of 7 or above. It would appear, therefore, that the phosphoric acid has the power to put out of action some toxic material even though the soil remains distinctly acid. It must be borne in mind, however, that 10 gms. of acid phosphate for 3.5 pounds of soil is an unusually heavy application.

The low yields obtained with aluminum sulfate and aluminum nitrate, in a soil having higher pH values than the acid phosphate treated pots, point strongly to the aluminum as a disturbing factor. This is in accord with the results obtained in the culture solution work.

It would appear that aluminum compounds may be precipitated quite as readily by the use of heavy applications of soluble phosphates as by the use of ground limestone, or other basic material. It is indeed quite possible that some of the benefit which in the past has been attributed to acid phosphate as a source of phosphorus for plants, should be credited to its ability to precipitate, and thus put out of action, soluble aluminum compounds.

It is very certain that in many cases, especially among potato growers, it has been used in quantities many times as large as required by the crop, and apparently with good results. *Its ability to put out of action such toxic compounds and at the same time maintain the soil in a rather acid condition, may account for its great value as a potato fertilizer.*

SUMMARY

Soils which had become toxic through more or less abnormal treatment were leached with distilled water and the leachings analyzed for soluble iron and aluminum and other constituents, and were also used as culture media for the growing of plants.

In growing the plants, portions of the extract were used unmodified, and other portions were modified by the addition of soluble phosphates, lime water and by adding ammonia, boiling and filtering to remove soluble iron and aluminum.

Normal soils were also extracted and the extract used in comparison with the extract from the toxic soil. The analyses of the extracts from the good and poor soil brought out differences in soil reaction, water-holding capacity, total nitrogen and carbon and water-soluble iron and aluminum.

The culture-solution work makes it very clear that there is something in the extract from the toxic soil which interferes with root development of the plants. The extract from the normal soil gave normal root development, as did the standard culture-solution.

Additions of nitrate of soda and small amounts of soluble phosphates to the extract from the toxic soil, did not correct the unfavorable condition to an appreciable extent.

When the toxic extract was boiled with ammonium hydroxide, filtered and a trace of iron and phosphoric acid added to the filtered solution, normal root and top growth were obtained.

That this improvement was not due entirely to the neutralizing of the acidity is shown by the fact that the standard control solution, which gave normal root growth, had a pH value approximately the same as the pH value of the toxic extract. Aluminum sulfate when added to normal culture solutions in amounts equivalent to, and greater than the Al_2O_3 present in the unmodified toxic extract, gave results similar to those with the unmodified extract. The pH values of the solutions were lowered by the addition of $Al_2(SO_4)_3$, but culture solutions brought to identically the same pH with H_2SO_4, produced plants much healthier in appearance than the cultures receiving the aluminum sulfate treatment. The results of the work point strongly to soluble aluminum as being responsible in part at least, for the unhealthy root development.

Vegetation tests carried out in small glazed earthenware pots gave results which confirm, in a large measure the culture-solution results. In the pot tests, however, heavy applications of acid phosphate to the toxic soil resulted in great improvement in growth even when the pH value was as low as 5. Small applications of soluble phosphates failed to give normal growth.

Heavy applications of ground limestone and basic slag gave good results in the pot experiments.

When aluminum compounds were introduced without a basic material such as lime, the yields were reduced to less than the yields with the untreated soil (check), but in the presence of liberal applications of basic materials, the aluminum sulfate and aluminum nitrate did not appreciably lower the yields of dry matter as compared with the yields from the basic materials without aluminum compounds.

The results of the pot work also lead one to suspect that soluble aluminum compounds constitute one of the causes of toxicity in soils.

The results of the work indicate that such toxicity may be largely overcome by heavy applications of soluble phosphates or by application of basic materials such as the different forms of lime and basic slag.

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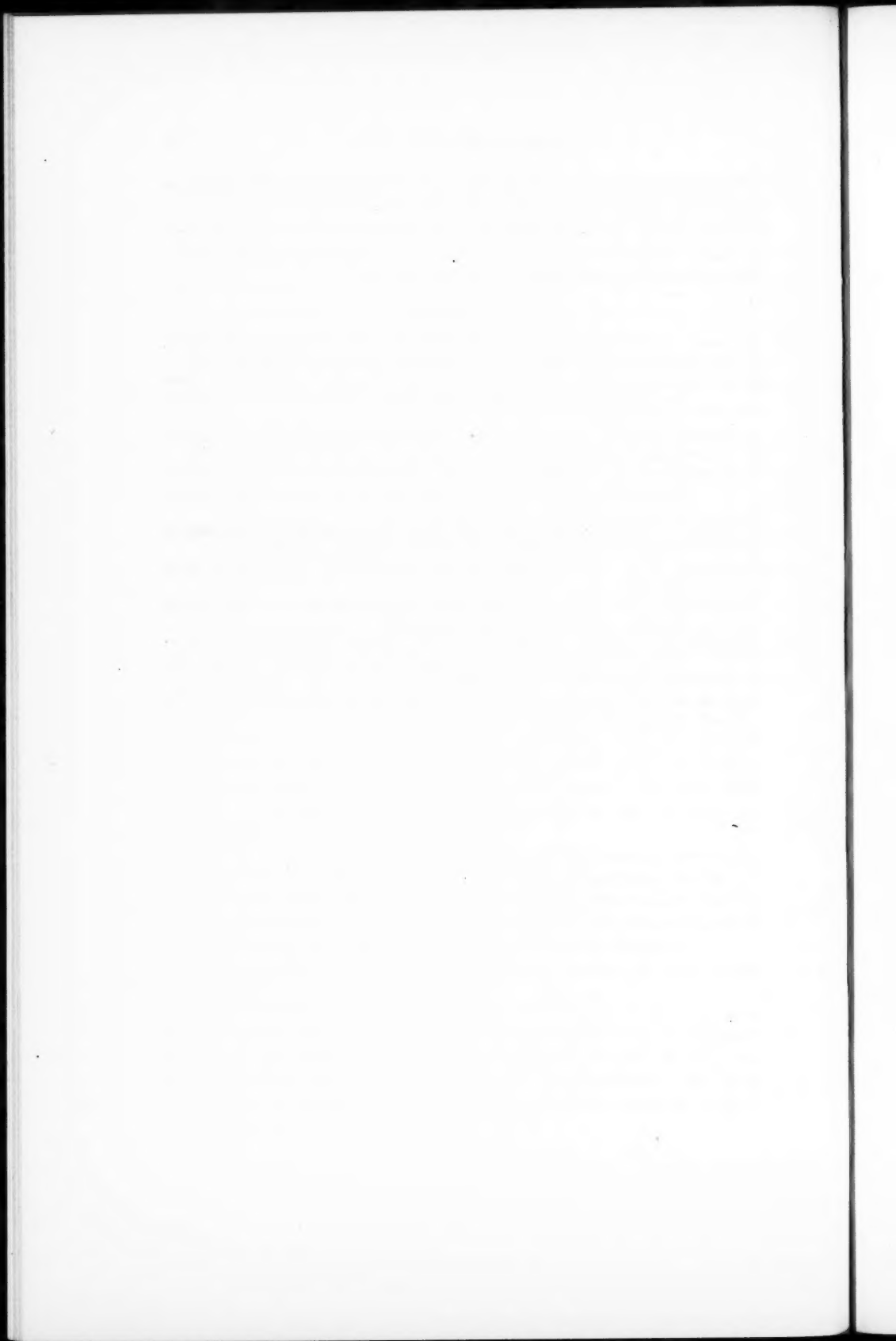
A METHOD FOR THE DETERMINATION OF "ACTIVE" ALUMINUM IN ACID SOILS[1]

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For many years the Rhode Island station has been studying the effects of "acid-soil" conditions, and more recently, of certain toxic substances resulting from or accompanying soil acidity, upon the growth of crop plants, and it has been shown that numerous plants are able to withstand fairly high concentrations of hydrogen ions in sand or water cultures, which are unable to produce any growth whatsoever in many soils of similar or even lower hydrogen-ion concentrations. One of the major reasons which has been advanced in explanation of these findings has been the presence of toxic concentrations of "active" aluminum salts in the acid, granitic soils under investigation (2, 3).

Sometime ago it became evident that a quantitative method of determining the actual concentrations of "active" aluminum in soils was necessary if further progress along these lines of study was to be made, and, with this end in view, a somewhat extended series of experiments was undertaken. Pure water, carbonated water, different concentrations of ammonium-chloride and nitrate solutions, and various normalities (1.0–0.01 N) of several of the more common organic and inorganic acids were all used in different proportions of soil to solvents, and shaken for different lengths of time. Aluminum determinations were made, using the solutions so obtained, and possible correlations between them and the growth of crop plants, known to be sensitive to "acid-soil" conditions were noted. Hydrogen-ion concentrations were also determined, using the soils employed and the solutions of the same, both before and after shaking. A full account of this work, together with other phases of the subject of aluminum toxicity to plants and its possible correction, will appear in a future publication from this station. The object of this brief paper is to describe the method finally adopted for the determination of "active" aluminum in soils, and to give reasons for its choice.

Neither pure water nor carbonated water dissolves sufficient quantities of aluminum, even from very acid soils, for accurate quantitative determination. The chief drawback to the use of a solution of a neutral salt, as ammonium chloride or ammonuum nitrate, is that the soils are here subjected to the solvent action of resulting solutions of different hydrogen-ion concentrations;

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the more acid the soil, the greater the absorption, or at least removal, of the cation, which in turn results in a solution of much higher hydrogen-ion concentration, and with it, a solution of greater dissolving power for aluminum. Our experimental work has shown that, when a very acid soil is shaken with a normal solution of ammonium chloride (1 of soil to 5 of solvent), a solution of pH 2–3 results, whereas, if the soil used is neutral or slightly alkaline, the ammonium-chloride solution remains unchanged (practically neutral) after agitation. The Hopkins method for determining soil acidity is, of course, based upon this phenomenon of absorption or chemical reaction as the case may be. As it seemed wise to employ a solvent having the same dissolving power for soil aluminum *irrespective of soil reaction*, ammonium-chloride solutions were finally discarded although data of some value were obtained prior to this action.

The fact that solutions of acetic and citric acids are but slightly dissociated and, when partially neutralized, progressively ionize to maintain a constant percentage or concentration of hydrogen ions, suggested to us the choice of a solvent which would probably remain constant in composition and hence in dissolving power, irrespective of the reaction of the soils employed. Normal, 0.5 N and 0.05 N solutions of these acids were thus made and soils of various reactions shaken therein. The pH values of these acid suspensions after shaking, and the aluminum contents of the same after being passed through a porcelain pressure filter were determined. It was soon found that the normal solutions made too strong an attack upon the soils, resulting in too large amounts of aluminum being dissolved to permit of a proper correlation with the growth of "aluminum-sensitive" plants. The 0.05 N solutions, on the other hand, were unable to maintain a constant hydrogen-ion concentration when shaken with soils of unlike reactions. The 0.5 N solutions, however, being between the two in strength, permitted a correlation with plant growth, besides maintaining a fairly constant hydrogen-ion concentration when agitated with soils of widely different reactions. Table 1 presents data in proof of certain of these contentions as secured with acetic acid. Citric acid yielded similar results but, on account of subsequent analytical difficulites, was abandoned in favor of acetic acid. All of the soils reported upon came from the field plots of the Rhode Island Station (Miami silt loam), the dissimilarity in reaction being due to past, long-continued differences in fertilizer and lime treatments.

A solvent of proper strength having been secured, the next step was to find an accurate method for determining the small amounts of aluminum present in the acetic acid soil extracts, which also carried considerable quantities of calcium, magnesium, potassium, phosphate, sulfate and nitrate ions, besides traces of iron, manganese, silicon and other, less common substances. The aluminum-hydroxide method of Blum was first tried, but it was found impossible so to regulate the hydrogen-ion concentration as to prevent the co-precipitation of small amounts of calcium phosphate. Colorimetric

methods, using alizarin-3 and hematoxylin, also received attention but were discarded as hardly meeting the standard of accuracy desired. The aluminum-phosphate method of Carnot,[2] somewhat modified, was finally adopted and has given uniformly good results in the presence of considerable quantities of the substances above enumerated. It has been carefully tested out, using standardized solutions of aluminum sulfate, and has given theoretical results even in the presence of rather large amounts of calcium and phosphate ions.

The detailed method at present used in this laboratory for the determination of "active" aluminum in soils follows:

Shake the equivalent of 100 gms. of dry soil for 1 hour with 500 cc. (minus the volume of water in the soil) of 0.5 N acetic acid in an end-over-end shaking machine (8 r.p.m.); allow to stand a few hours or over night to settle, and then filter the supernatant liquid through

TABLE 1

Hydrogen-ion concentration of soils as affecting both the amounts of aluminum dissolved there-from by different strengths of acetic acid and the hydrogen-ion concentrations of the suspensions after agitation

REACTION OF SOIL USED	REACTION OF ACETIC ACID SUSPENSION AFTER AGITATION	Al_2O_3 IN DRY SOIL
Normal acetic acid		
pH	pH	*p.p.m.*
4.5	2.6	1100
6.1	2.8	350
7.8	2.9	197
0.5 N acetic acid		
4.5	3.0	812
5.5	3.1	650
6.1	3.2	344
7.0	3.4	314
7.8	3.4	135
0.05 N acetic acid		
4.5	3.4	361
6.1	3.9	260
6.7	4.2	Trace
7.0	4.4	....

[2] Since this paper was written, Lundell and Knowles (4) have published results of a careful study of the several factors which influence the accuracy of this method. They give direc-tions for precipitation and washing which are closely in accord with those which have been followed in our laboratory for the past year. The only points of difference between their method and ours are that they use macerated filter paper during the precipitation of the aluminum phosphate, and that, prior to the first precipitation, we boil with sodium thio-sulfate to reduce the traces of ferric iron usually present in soil extracts. The small amounts of titanium ordinarily present in soils are not soluble in 0.5 N acetic acid.

a Pasteur-Chamberland unglazed porcelain tube under pressure. Evaporate exactly 250 cc. of this filtrate to dryness (first on the hot plate and then on the water bath) after adding 10 cc. of aqua regia. Moisten the residue with 10 to 15 cc. of 1-to-1 hydrochloric acid and evaporate to dryness twice to dehydrate completely the silicon hydroxide. Finally digest the residue in about 100 cc. of hot, dilute hydrochloric acid and filter, washing the filter paper free from chlorides with hot water. To this filtrate containing the aluminum (which should measure about 200 cc.) add a decided excess of ammonium phosphate (5 cc. of a 10 per cent solution), and bring to a boil. Add 2 cc. of normal sodium thiosulfate solution and continue boiling for at least 10 minutes to reduce completely any ferric iron that may be present (ferrous phosphate is soluble in acetic acid). *Just* neutralize (use litmus paper) with $NH_4(OH)$, avoiding any excess, and immediately acidify very slightly[3] with a few drops of a 50-per cent solution of acetic acid. Boil, let precipitate subside, and filter. Wash precipitate once with hot water and dissolve the aluminum phosphate from the free sulfur on the filter with hot, dilute (1 to 6) hydrochloric acid, refiltering if solution at first comes through turbid. Wash the filter with hot water until free from chlorids (about 200 cc.). Reprecipitate the aluminum phosphate by adding first to the hot filtrate 5 cc. of the 10 per cent ammonium-phosphate solution, then dilute NH_4OH until a *slight* permanent precipitate *just begins* to form, and then 10 cc. of a 15 per cent solution of ammonium acetate (the hot solution should test slightly acid with litmus paper at this point). Boil and filter as above; wash free from chlorides with hot water; ignite the $AlPO_4$ to a constant weight. Multiply the weight of the $AlPO_4$ precipitate, in grams, by 8370. This gives parts per million of Al_2O_3 on the dry soil basis. A third precipitation may be necessary to separate completely the calcium and aluminum phosphates where the soils employed have received recently large dressings of either acid phosphate or lime.

Data have been obtained which show that air-drying acid soil increases the amounts of aluminum dissolved therefrom, by 15–20 per cent, hence it is advisable to use soil fresh from the field where possible.

Table 2 presents a few data selected from among many such, which show the existence of certain correlations between the reactions of the soils studied, the amounts of aluminum as determined by the above method, and the growth of plants known to be especially sensitive to "acid-soil" conditions. These crops were grown in Wagner pots in soils from differently treated field plots, and for the two crops here given, were all similarly fertilized in the pots, immediately prior to planting, with moderate applications of sodium nitrate, potassium sulfate and acid phosphate. The onion crop followed the let tucecrop in the same soils. The yields are averages from duplicate pots. This table shows a definite relationship between the amounts of "active" aluminum as here determined, soil reaction and crop growth. On the type of granitic soil here studied (over 80 per cent insoluble matter) and on others of similar composition and origin, data have been secured which show that, in the presence of 0.5 N acetic acid but irrespective of hydrogen ion concentration, soluble alumina in excess of approximately 225 p.p.m. of dry soil renders such soils somewhat toxic to crops which are especially sensitive to so-called "acid-soil" conditions.

In table 3 are tabulated a few results secured from three greenhouse beds of

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[3] If the solution at this point is made too strongly acid, a slight loss (about 30 p.p.m. of alumina) will result, as $AlPO_4$ is slightly soluble in strong acetic-acid solutions (from 3 to 4 mgm. per 100 cc. of solvent).

lettuce. These beds are each approximately 0.0005 acre in area. The soil came originally from one of the acid experimental plots, but has since been heavily limed in each case. Besides lime, Bed 3 has received ordinary applications of acid phosphate, and Bed 6, heavy applications of well rotted compost. The yields given are for entire beds.

TABLE 2

Correlation of "active" aluminum, soil reaction and crop growth

SOIL NUMBER	REACTION OF SOIL	"LIME REQUIRE-MENT" PER 2,000,000 POUNDS OF SOIL*	Al₂O₃ IN DRY SOIL	WEIGHT OF FRESH CROPS	
				Cos lettuce	Yellow globe onions
	pH	*lbs. of CaO*	*p.p.m.*	*gm.*	*gm.*
1	4.5	4410	812	0	0
3	4.7	3780	731	1	0
5	5.5	2520	650	24	0
6	6.1	1440	344	59	117
9	6.6	1170	290	77	197
10	7.0	720	314	78	256
14	7.8	450	135	127	240

* Jones method as modified by the writer (1, p. 9).

It should be stated that, although Beds 3 and 4 had recently received a dressing of finely ground limestone equivalent to about 20 tons per acre, it had not completely reacted with the soil, as many small, white particles of calcium carbonate were readily discernible in the soil mass. These data— and they are substantiated by other of our experiments—would indicate that *lime alone* is unable to precipitate *entirely* all of the soluble aluminum present in the complex soil solutions of very acid soils when unaccompanied by fairly large applications of soluble phosphate.

TABLE 3

"Active" aluminum as influencing lettuce yields in greenhouse soils

BED NUMBER	REACTION OF SOIL	Al₂O₃ IN DRY SOIL	WEIGHT OF GREEN LETTUCE HEADS
	pH	*p.p.m.*	*gm.*
3	7.0	240	2270
4	7.0	82	5516
6	7.2	46	7105

In conclusion it should be stated that the data given in this paper are some-what fragmentary, having been chosen from a considerable amount of similar material, and have been advanced simply to show the reasons for the adoption as well as the practical value of this method for determining "active" aluminum in agricultural soils.

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THE EFFECT OF GYPSUM ON IOWA SOILS[1]

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Investigations dealing with the amount of sulfur in soils and crops and the loss of this constituent from soils, which have appeared in the literature in the last decade, have caused a renewed activity on the part of scientists to study the relation of sulfur to soil fertility.

Many analyses of soils have been made in various parts of the country and the sulfur supply has been found to be low in most cases. Crops remove considerable amounts of sulfates and there is apparently a large loss of the element in the drainage water. The importance of studying the sulfur problem and the relation of sulfur to soil fertility is evident. Since gypsum supplies this element in an available form it is only natural that the material should be considered with other sulfur fertilizers, and experiments are necessary to determine its actual value.

The present work was planned to determine first, the chemical and bacterial effects of gypsum on Iowa soils; and second, to study the effect of gypsum on crop growth and protein content of crops on various Iowa soils under different conditions.

PART I. THE CHEMICAL AND BACTERIAL EFFECTS OF GYPSUM IN SOIL

THE EFFECT OF GYPSUM ON PHOSPHORUS AND POTASSIUM

Six 500-gm. portions of air-dry sieved soil of each of six important Iowa soil types were placed in 1-pint mason jars. Gypsum was added at the rate of 200 and 20,000 pounds per acre to duplicate jars and two of each type were untreated. Distilled water was added to bring the content up to the optimum. The jars were covered and kept at room temperature for seven months, water being added at frequent intervals to keep up the content. At the end of that time the soils were air-dried and analyzed for water-soluble phosphorus and potassium. The results of these analyses and the total phosphorus and potassium content of each soil are given in table 1.

The Shelby loam, having only 525 pounds of total phosphorus per acre, showed the largest amount of water-soluble phosphorus of any of the soils.

With this soil the 200-pound gypsum treatment caused a slight increase in water-soluble phosphorus, whereas the 20,000 pound treatment decreased the solubility.   With the Marshall silt loam the small application of gypsum increased slightly the solubility of the soil phosphorus while the heavy treatment had no effect whatever. Neither of the gypsum treatments exerted any effect on the phosphorus of the Carrington loam. The 200-pound gypsum

TABLE 1

Total and water-soluble phosphorus and potassium of six soil types treated with gypsum

NUMBER	SOIL TYPE AND TREATMENT PER ACRE	PHOSPHORUS PER ACRE[*]		POTASSIUM PER ACRE[*]	
		Total	Water-soluble	Total	Water-soluble
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*
	Shelby loam:				
1	Check..........................	525	6.47	18,202	49.20
2	Gypsum 200.....................	525	7.27	18,202	48.24
3	Gypsum 20,000..................	525	4.58	18,202	130.24
	Marshall silt loam:				
4	Check..........................	1347	4.58	35,376	47.27
5	Gypsum 200.....................	1347	5.65	35,376	33.76
6	Gypsum 20,000..................	1347	4.58	35,376	124.13
	Carrington loam:				
7	Check..........................	1037	4.58	29,201	40.20
8	Gypsum 200.....................	1037	4.58	29,201	43.09
9	Gypsum 20,000..................	1037	4.58	29,201	149.22
	Webster loam:				
10	Check..........................	848	3.77	24,377	45.94
11	Gypsum 200.....................	848	4.04	24,377	28.62
12	Gypsum 20,000..................	848	3.77	24,377	164.65
	Clinton silt loam:				
13	Check..........................	956	3.77	31,131	54.67
14	Gypsum 200.....................	956	4.04	31,131	35.69
15	Gypsum 20,000..................	956	4.04	31,131	111.59
	Tama silt loam:				
16	Check..........................	1535	5.38	31,516	65.28
17	Gypsum 200.....................	1535	7.27	31,516	60.78
18	Gypsum 20,000..................	1535	5.38	31,516	155.33

[*] Calculated on the basis of 2,000,000 lbs. of soil.

treatment increased the water-soluble phosphorus of the Webster loam, but the difference was too small to be significant.   The effects of the gypsum on the Clinton silt loam were likewise negligible.   An increase of almost 2 pounds of soluble phosphorus was brought about by the small amount of gypsum on the Tama silt loam, but the larger treatment showed no effect.

Considering all the results, it is evident that the heavy application of gypsum had no effect on the content of water-soluble phosphorus of these soils while the 200-pound treatment gave a slight, though unmistakable, increase in all the soils studied except the Carrington loam.

The water-soluble potassium obtained from the 200-pound gypsum treatment was less in all the soils, except one, than that extracted from the untreated soils. The one exception was the Carrington loam. These results are exactly the opposite of those for water-soluble phosphorus.

The excessive gypsum treatment brought about a decided increase in the solubility of the potassium, in each soil type studied, the amount of potassium in the water extracts varying with the type of soil. There seems to be no question but that gypsum in large amounts may have a marked solvent action on the native soil potassium.

A second experiment to determine the effect of gypsum on phosphorus and potassium, was carried out on a neutral Carrington loam which had been used in a previous experiment to test the effect of gypsum on soil reaction. Gypsum had been added to this soil with and without $CaCO_3$, and the pots had been maintained at the optimum moisture-content for a period of five

TABLE 2

Total, water-soluble, and ammonium-citrate-soluble phosphorus and potassium per acre*

TREATMENT OF NEUTRAL SOIL	TOTAL		WATER-SOLUBLE		AMMONIUM-CITRATE-SOLUBLE	
	Phosphorus	Potassium	Phosphorus	Potassium	Phosphorus	Potassium
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Check	1454	27,079	23.16	80.40	370.42	3069.28
500 lbs. gypsun...........................	1454	27,079	19.39	109.98	404.10	1849.20
4000 lbs. calcium carbonate................	1454	27,079	22.09	81.04	377.18	2934.60
4000 lbs. $CaCO_3$ plus 500 lbs. gypsum........	1454	27,079	24.78	101.62	437.78	3344.64

* Calculated on the basis of 2,000,000 lbs. of soil.

months. The soils were air-dried and analyzed for total, water-soluble and ammonium-citrate-soluble phosphorus and potassium. The results of these analyses are shown in table 2.

The gypsum when used alone seemed to cause a decrease in the solubility of phosphorus in water but when used with $CaCO_3$ a slight increase was found. Lime alone had no effect on the phosphorus. Gypsum used with and without $CaCO_3$ increased the amount of phosphorus dissolving in ammonium-citrate solution the larger amount being obtained when the $CaCO_3$ was used. The $CaCO_3$ treatment alone had no effect on the citrate-soluble phosphorus.

The 500-pound application of gypsum with or without lime caused a decided increase in the solubility of potassium while the $CaCO_3$ alone had no effect.

The results for the ammonium-citrate soluble potassium were similar to those obtained for the water-soluble potassium, with the exception of the 500-pound gypsum treatment which decreased the soluble potassium.

To check the laboratory results by actual field tests, six square-rod plots were laid out in 1921 on a clover field on Carrington loam and treated with

different amounts of gypsum on May 9. Three months later a composite soil sample was taken from each plot and analyses were made for total, water-soluble, and ammonium-citrate-soluble phosphorus and potassium. The results are given in table 3.

The smallest application of gypsum effected a slight decrease in water-soluble phosphorus, while the 1000-pound gypsum treatment apparently caused a slight increase. The other treatments had no effect and it seems that gypsum did not have any influence on the water-soluble phosphorus in this soil. In the case of the ammonium-citrate-soluble phosphorus, the 200-pound gypsum treatment slightly increased the quantity of phosphorus going into solution, while the 1000 pounds of gypsum had no effect. The results of the 200 and 2000 pound gypsum treatments were not definite.

TABLE 3

The effect of gypsum on phosphorus and potassium. 1-square-rod plots treated with different amounts of gypsum

TREATMENT PER ACRE	TOTAL		WATER-SOLUBLE		CITRATE-SOLUBLE	
	Phos-phorus	Potassium	Phos-phorus	Potassium	Phos-phorus	Potassium
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Nothing......................	1023	28,979	22.90	45.02	343.48	127.03
200 lbs. gypsum...............	1050	28,979	21.56	57.88	356.96	286.22
500 lbs. gypsum...............	1050	28,979	22.90	78.89	356.96	184.92
1000 lbs. gypsum..............	1050	28,979	24.24	91.65	343.48	220.29
2000 lbs. gypsum..............	996	28,979	22.90	184.92	323.28	247.63
Nothing......................	1023	28,979	22.90	41.80	343.48	144.72

Turning to the results for potassium it appears that each gypsum treatment effected a marked solubility in the soil potassium, the amount of potassium going into solution increasing with the larger additions of gypsum. The ammonium-citrate-soluble potassium determinations also show an unmistakable increase in the solubility of the soil potassium with gypsum. The increase was not proportional to the amount of gypsum added, however, the smallest treatment showing the greatest increase.

From these tests, it may be concluded that gypsum in small amounts may increase the solubility of the phosphorus and potassium in some soils. In others, no effects may appear. Excessive applications, however, have a large effect on the solubility of the soil potassium.

THE EFFECT OF GYPSUM ON NITROGEN

The effect of gypsum on the nitrogen transformations taking place in the soil was determined by measuring certain bacterial activities in a soil treated with different amounts of gypsum. Determinations were made at regular intervals for the ammonifying, nitrifying and azofying powers of the soil. For these experiments a neutral Carrington loam was selected.

Eighteen 4-gallon glazed earthenware pots were filled with 36 pounds of fresh soil containing 17 per cent moisture. Gypsum was applied to duplicate pots at the rate of 100, 200, 500, 1000, 1500, 2000, 5000 and 10,000 pounds per acre, thoroughly mixed with the soil and the moisture-content was then brought up to the optimum (23%) and kept at that point during the experiment.

The ammonifying power of the soils was determined in 100-gm. portions in tumblers with 5 gm. of dried blood. The incubation period was seven days and the ammonia was determined by the aeration method with Na_2CO_3. Nitrification was determined in air-dry soils also, with 100 mgm. $(NH_4)_2SO_4$. The incubation period was 4 weeks and the phenol-disulfonic-acid method was used to measure the nitrates.

Azofication was determined in a sterile dextrose solution, inoculating with infusions of fresh soil (1 cc. of infusion of 50 gm. soil to 100 cc. water, shaken 5 minutes). The nitrogen fixed was determined by the regular Kjeldahl method and the results are expressed as nitrogen fixed per gram of dextrose.

Two weeks after the experiment was started samples were drawn from each pot and tested for their ammonifying, nitrifying, and azofying power. The second and third samplings were made at two week intervals while the fourth, fifth and sixth samplings were taken at monthly intervals.

TABLE 4

Effect of gypsum on ammonification

POT NUMBER	GYPSUM APPLIED	NH₃ PER 100 GM. AIR-DRY SOIL				
		1st sampling	2d sampling	3d sampling	4th sampling	5th sampling
	lbs.	mgm.	mgm.	mgm.	mgm.	mgm.
1, 2	Check	137.5	148.9	166.7	176.1	149.8
3, 4	100	127.6	156.6	171.4	172.9	155.3
5, 6	200	119.2	147.1	158.7	168.7	157.3
7, 8	500	118.4	142.8	155.6	151.1	134.7
9, 10	1,000	141.2	139.0	133.7	134.5	128.2
11, 12	1,500	142.5	139.5	135.5	141.7	132.8
13, 14	2,000	145.3	139.7	135.1	138.3	138.0
15, 16	5,000	145.1	144.3	121.5	137.4	126.5
17, 18	10,000	127.5	124.5	120.1	133.6	115.5

THE EFFECT OF GYPSUM ON AMMONIFICATION

The results of the tests for ammonification are shown in table 4.

At the first sampling, the 100-, 200-, 500-, and 10,000-pound treatments with gypsum depressed the ammonifying power of the soil, but the remaining treatments showed a slight increase in ammonia production. At the next three samplings in all cases except the 100-pound treatment, gypsum had a depressing effect on ammonification. The 100-pound gypsum application favored ammonification at the second and third samplings. At the fourth sampling the smallest treatment with gypsum gave a slight reduction in the amount of ammonia produced. Both the 100- and 200-pound gypsum treatments favored ammonification at the fifth sampling.

An average of the five samplings shows that the check produced 155.8 mgm. nitrogen; the 100 pounds of gypsum, 156.7 mgm.; and the 200-pound treatment, 150.2 mgm. as ammonia. It seems therefore that the 100- and 200-

pound applications of gypsum had no effect on the ammonifying power of this soil, and used at the rate of 500 to 10,000 pounds per acre it exerted an unfavorable effect on ammonification.

THE EFFECT OF GYPSUM ON NITRIFICATION

The nitrates present in the soils at the different samplings are shown in table 5.

There was considerable variation in nitrates present at the different samplings and therefore only the average of the five samplings will be discussed. The 2000- and 5000-pound gypsum treatments were the only ones which

TABLE 5

Nitrates in soils at various samplins

POT NUMBER	GYPSUM APPLIED	NITRATE NITROGEN IN 100 GM. AIR-DRY SOIL					
		1st sampling	2d sampling	3d sampling	4th sampling	5th sampling	Average
	lbs.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1, 2	Check	2.15	1.07	0.94	1.28	0.85	1.26
3, 4	100	2.23	1.19	1.03	1.55	0.95	1.39
5, 6	200	2.14	0.90	0.97	1.45	0.69	1.23
7, 8	500	1.70	1.06	1.01	1.22	0.70	1.14
9, 10	1,000	1.77	0.85	0.95	1.33	1.07	1.19
11, 12	1,500	1.88	0.92	1.01	1.25	1.14	1.24
13, 14	2,000	0.95	0.87	0.69	1.04	0.98	0.91
15, 16	5,000	0.66	0.88	0.74	1.08	1.06	0.88
17, 18	10,000	2.53	2.28	1.94	2.00	1.58	2.07

caused any appreciable decrease in the amount of nitrates present. The 100-pound application evidently favored nitrification in the soil although the increase was small. The largest application of gypsum, 10,000 pounds, showed a decided gain in nitrate nitrogen.

The results showing the effect of gypsum on nitrification appear in table 6.

At the first sampling, all of the gypsum treatments produced an unfavorable influence on the nitrification of ammonium sulfate, the depression being approximately the same for all treatments. At the second sampling the first four gypsum treatments were apparently favorable to the nitrifying bacteria for there was a decided gain in the nitrate nitrogen produced. The remaining treatments manifested a slightly harmful influence on nitrification.

At the third sampling, a slight decrease in nitrate nitrogen occurred with all the treatments except the 100-pound application. This was true also at the fourth sampling. At the fifth sampling, all of the soils produced practically the same amount of nitrate nitrogen.

Considering the general average of all the samplings, it is evident that gypsum when used in amounts from 100 to 1000 pounds per acre exerted no appreciable effect on the nitrification of ammonium sulfate, while larger applications of 1500, to 10,000 pounds per acre had a slightly depressing effect.

THE EFFECT OF GYPSUM ON AZOFICATION

In table 7 appear the results for the azofication tests. Although the amounts of nitrogen fixed per gram of dextrose were exceedingly small the results for the different samplings agree very well. The largest amount of nitrogen was fixed by the untreated soil, in every case except at the second sampling. Except with the 100-pound application at this sampling, all of the gypsum treatments apparently decreased the amount of nitrogen fixed in the solutions. The amount of fixation decreased as the size of the gypsum treatment was increased and the 10,000-pound application almost inhibited azofication.

TABLE 6

The effect of gypsum on nitrification

POT NUMBER	GYPSUM APPLIED	NITRATE NITROGEN IN 100 GM. OF AIR-DRY SOIL					
		1st sampling	2d sampling	3d sampling	4th sampling	5th sampling	General Average
	lbs.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1, 2	Check	15.2	16.6	16.6	15.4	20.0	16.8
3, 4	100	13.0	18.6	16.6	15.4	20.0	16.7
5, 6	200	13.3	19.0	15.9	14.1	19.1	16.3
7, 8	500	13.6	18.2	14.7	14.1	18.3	15.8
9, 10	1,000	13.6	19.6	13.9	14.2	19.1	16.1
11, 12	1,500	14.0	15.4	14.2	13.7	17.4	14.9
13, 14	2,000	13.8	16.4	13.3	13.3	19.1	15.2
15, 16	5,000	12.9	13.6	14.1	14.9	19.1	14.9
17, 18	10,000	12.9	15.7	15.2	14.2	20.0	15.6

The samples taken at the fourth and fifth samplings were not tested for their azofying power. It was believed at the time that sufficient data had been secured to reach a definite conclusion on the effect of gypsum on azofication. It was thought, however, that the results might have been different had mannitol been used instead of dextrose and consequently at the sixth sampling, tests were made using mannitol instead of dextrose in the medium. The data given for the sixth sampling are very much the same as those obtained at the first three samplings. Dextrose, therefore, is apparently just as good as the more expensive mannitol for measuring the relative nitrogen-fixing power of variously treated soils.

THE EFFECT OF GYPSUM ON ORGANIC MATTER

In order to determine the effect of gypsum on organic matter in the soil the following experiment was planned:

Three soils were obtained from different locations in the Wisconsin drift soil area, and all were classed as Carrington loam. The first soil had a lime requirement of 2260 pounds of $CaCO_3$ per acre as determined by the modified Tacke method. The second soil was neutral in reaction and the third soil was highly basic, containing a large amount of calcium bicarbonate.

Twelve 500-gm. portions of each soil (air-dry) were weighed out in 800-cc. shaker-bottles, ground clover hay was added to each at the rate of 2 tons per acre and gypsum was applied in varying amounts as shown in table 8.

A layer (¾ inch thick) of CO_2-free fine gravel was first placed in the bottom of each bottle to permit even distribution of air through the soil. The moisture-content of the soils was adjusted to the optimum. The detailed arrangement of the carbon dioxide apparatus as described by Potter and Snyder, was followed in all its essential details. The system contained 24 bottles and likewise 24 carbon dioxide absorption towers, and only two soils were run at one time. During the early part of the experiment, titrations for carbon dioxide were made twice a week. Later once a week was all that was necessary. When the first two soils had ceased to evolve significant amounts of carbon dioxide, another series was started.

The total carbon dioxide production for each treatment for the entiré period of experimentation is given in table 8; the individual results are not shown.

TABLE 7

The effect of gypsum on azofication

POT NUMBER	GYPSUM APPLIED	NITROGEN FIXED PER GRAM OF DEXTROSE				
		1st sampling	2d sampling	3d sampling	6th sampling	General average
	lbs.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1, 2	Check	4.4	1.7	2.1	4.0	3.06
3, 4	100	3.8	3.2	1.6	1.9	2.62
5, 6	200	3.2	2.1	1.4	2.6	2.32
7, 8	500	1.5	1.7	1.0	1.3	1.37
9, 10	1,000	0.9	1.3	1.1	1.3	1.15
11, 12	1,500	1.0	1.1	0.9	0.9	0.97
13, 14	2,000	0.7	1.7	1.0	1.5	1.22
15, 16	5,000	0.7	1.0	1.0	0.6	0.82
17, 18	10,000	0.5	1.4	0.8	0.1	0.70

The 100-pound gypsum treatment apparently had no effect on the carbon dioxide production in the acid soil. The 200-, 500-, and 1000-pound applications showed slight decreases in CO_2 production but the differences were not large enough to be significant and the duplicates did not agree exactly. The 2000-pound treatment caused an increase in CO_2 evolution, but the duplicates did not agree and one of them was almost the same as the check.

In the case of the neutral soil, the 100-, 200-, and 500-pound gypsum treatments showed practically the same amount of carbon dioxide production as the check soil.

The 1000-pound gypsum treatment was considerably higher than the first three treatments. The largest gypsum treatment showed a low production of CO_2 but since one of the duplicates was lost no definite conclusion should be drawn.

With the basic soil, all of the treatments produced a decided increase in CO_2 evolution with the exception of the 500-pound application and with this treatment there was no effect.

It is well known that the addition of $CaCO_3$ to a soil high in organic matter causes a considerable increase in CO_2 evolution. An experiment was run to determine the effect of gypsum on CO_2 production when used with lime and organic matter. The acid soil used in the earlier test was employed for this work and the results are given in table 9.

TABLE 8
The effect of gypsum on carbon dioxide

POT NUMBER	GYPSUM APPLIED	CARBON DIOXIDE PRODUCED		
		Acid soil	Neutral soil	Basic soil
*	lbs.	mgm.	mgm.	mgm.
1, 2	Check	1595	1563	1579
3, 4	100	1605	1565	1663
5, 6	200	1517	1533	1618
7, 8	500	1564	1543	1554
9, 10	1000	1561	1639	1633
11, 12	2000	1671	1424	1690

Where no clover was added, the amount of CO_2 produced was considerably less than for the clover treatment alone. Gypsum applied alone at the rate of 1000 pounds per acre decreased the amount of CO_2 evolved and the soils receiving $CaCO_3$ increased CO_2 evolution to a marked degree. The 200- and 1000-pound applications of gypsum with the lime had no effect on the CO_2 produced.

TABLE 9
The effect of gypsum and lime on carbon dioxide production

NUMBER	TREATMENT	CARBON DIOXIDE PRODUCED
		mgm.
1, 2	Check...	1155
3, 4	2 T. clover..	1630
5, 6	2 T. clover and 2 T. lime..........................	2008
7, 8	2 T. clover, 2 T. lime and 200 lbs. gypsum..............	1990
9, 10	2 T. clover, 2 T. lime and 1000 lbs. gypsum..............	2024
11, 12	1,000 lbs. gypsum..................................	956

The work reported here would seem to warrant the conclusion that the use of gypsum in amounts employed in ordinary practice apparently had no effect on those types of bacteria that are active in breaking down the soil organic matter with the liberation of carbon dioxide. No effect was shown on the ammonifiers and nitrifiers and hence gypsum under the conditions of these experiments gave no indications of being a so-called "soil stimulant." Its indirect action on the soil must be attributed to chemical action rather than to an effect on bacterial activities.

Part II. The Effect of Gypsum on Crop Growth and Protein Content of Crops

In the spring of 1920, a number of field experiments were started to test the effect of gypsum on different crops when grown on various soil types in Iowa. A series of nine plots was laid out on fields in Story, Webster, Hardin and Wapello counties. The first three fields were located on Carrington loam, and the Wapello county field was on the Grundy silt loam. Gypsum was applied about May 1, 1920 to these plots at the rate of 200, 500 and 1000 pounds per acre with and without lime.

The plots were all $\frac{1}{10}$ acre except those in Story county which were $\frac{1}{40}$ acre in size. These fields were located near Ames, Fort Dodge, Eldora, and Farson. The first three fields mentioned were planted with oats, seeded to clover while the Farson field was planted to wheat, seeded to clover.

In a number of counties two $\frac{1}{10}$-acre plots were extended from a regular series of experimental plots belonging to the Soils Section of the Iowa Agricultural Experiment Station. This arrangement was made in Clinton, Scott, Lee, Buena Vista, Wapello and Van Buren counties. These fields are designated Delmar (Muscatine silt loam), Eldridge (Muscatine silt loam), Sawyer (Grundy silt loam), Truesdale (Carrington loam), Agency (Grundy silt loam) and Stockport (Grundy clay loam), respectively. The treatment for these two plots was 500 pounds of gypsum with and without limestone, except on the Agency and Stockport fields which received gypsum at the rate of 200 and 500 pounds per acre on clover in 1921.

In the spring of 1920 the Delmar and Eldridge fields were seeded to barley, and the Sawyer and Truesdale fields were seeded to oats. Four tons of ground limestone were applied with the gypsum treatment at the Truesdale field. Lime was applied to the Sawyer field after the oats were harvested.

The original plan of rotation called for each of these fields to be in clover in 1921. Unfortunately only three, Truesdale, Agency and Stockport, yielded clover in 1921. The Sawyer field was seeded to rye in 1921; the Delmar field was seeded to wheat; and the clover on the Eldridge field was plowed under early in the spring of 1921 for corn. No results for 1921 were obtained for these last two fields.

THE EFFECT OF GYPSUM ON SMALL GRAINS

The results showing the effect of gypsum on oats at the Ames, Fort Dodge and Eldora fields are given in table 10. No records were obtained from the wheat plots at the Farson field.

On the Ames experimental field the gypsum treatments had practically no effect on the oats. Slight gains were noted in the case of the 500 and 1000 pound gypsum treatments with lime, but these were too small to be significant.

On the Fort Dodge field 200 pounds of gypsum gave an increase of 11.9 bushels of oats per acre over the average of the two check plots. The plot receiving lime alone was low and therefore no comparison can be made between it and the three plots receiving lime and gypsum.

On the Eldora field the gypsum caused a noticeable increase in oats. The 200 pound application gave a gain of 8.2 bushels of oats; 500 pounds, a gain of 4.8 bushels, while the plot receiving the large application of gypsum showed an increase of 15 bushels per acre when compared with the first check plot.

The plot with 500 pounds of gypsum and lime showed an increase of 10.9 bushels per acre over the plot receiving lime alone while the 200- and 1000-pound gypsum treatments with lime showed only small increases. The yields for the second check plot were rather high and made comparisons difficult.

TABLE 10

The effect of gypsum on yield of oats per acre

PLOT NUMBER	TREATMENT	CARRINGTON LOAM		
		Ames	Fort Dodge	Eldora
		bu.	bu.	bu.
1	Check......................................	44.2	52.4	48.3
2	200 lbs. gypsum...........................	44.2	66.0	56.5
3	500 lbs. gypsum...........................	46.6	56.5	53.1
4	1000 lbs. gypsum..........................	46.3	51.0	63.3
5	200 lbs. gypsum and lime..................	44.5	57.8	57.8
6	500 lbs. gypsum and lime..................	46.6	57.8	65.3
7	1000 lbs. gypsum and lime.................	49.0	61.9	55.1
8	Lime......................................	47.6	46.9	54.1
9	Check......................................	44.2	55.8	61.9

The results showing the effect of gypsum on barley, oats and rye at the Delmar, Eldridge, Truesdale and Sawyer fields are given in table 11.

On the Delmar field one of the treatments with gypsum yielded a gain of 3.1 bushels of barley per acre while the duplicate plot gave no increase, hence no conclusions are possible. On the Eldridge field the two gypsum plots showed a slight increase in amount of barley produced.

TABLE 11

The effect of gypsum on yield per acre of barley, oats and rye

PLOT NUMBER	TREATMENT	MUSCATINE SILT LOAM		CARRING-TON LOAM	GRUNDY SILT LOAM	
		Delmar (barley)	Eldridge (barley)	Truesdale (oats)	Sawyer (oats)	Sawyer (rye)
		bu.	bu.	bu.	bu.	bu.
1	Check........................	24.5	19.0	56.5	34.3	20.9
2	500 lbs. gypsum...............	24.5	23.6	56.1	50.9	31.5
3	500 lbs. gypsum...............	27.6	21.8	....	61.1	....
4	500 lbs. gypsum and lime.........	....	....	59.2	....	24.2

Gypsum used alone did not have any effect on the production of oats on the Truesdale field but with lime a small gain was secured.

On the Sawyer field gypsum effected a marked increase in the production of oats. The average increase for the two plots over the check plot was 21.7 bushels per acre. In 1921 on this same field gypsum alone increased the yield of rye by 10.6 bushels while with lime the increase was only 2.3 bushels.

THE EFFECT OF GYPSUM ON RED CLOVER

The clover hay was harvested from each entire plot at Ames but on the other fields a strip was cut across each plot, measuring 1/30 of an acre, and the yields were calculated from this area.

The results of the 1921 red clover hay yields on the Ames, Fort Dodge, Eldora and Farson fields are found in table 12.

TABLE 12

The effect of gypsum on yield of red clover per acre

PLOT NUMBER	TREATMENT	CARRINGTON LOAM			GRUNDY SILT LOAM
		Ames	Fort Dodge	Eldora	Farson
		lbs.	lbs.	lbs.	lbs.
1	Check...........................	3000	2960	4620	4030
2	200 lbs. gypsum.....................	3440	3220	4860	4070
3	500 lbs. gypsum.....................	3472	3270	4470	4490
4	1000 lbs. gypsum...................	3840	3340	3390	4140
5	200 lbs. gypsum and lime..............	3760	2750	5400	5520
6	500 lbs. gypsum and lime..............	3140	2860	5460	5310
7	1000 lbs. gypsum and lime.............	3100	2750	6720	5140
8	Lime..............................	2952	3120	5310	4520
9	Check...........................	3260	4000	5970	4760

Gypsum was favorable to red clover on the Ames field. The 200-pound application increased the yield by 400 pounds. The 500-pound treatment produced only a slightly greater increase than the 200-pound application, but the plot receiving 1000 pounds of gypsum per acre increased the yield

TABLE 13

The effect of gypsum on yield of red clover per acre

PLOT NUMBER	TREATMENT	CARRINGTON LOAM TRUESDALE	GRUNDY SILT LOAM AGENCY	GRUNDY CLAY LOAM STOCKPORT
		lbs.	lbs.	lbs.
1	Check...........................	4268	4657	2272
2	200 lbs. gypsum...................	....	4830	2176
3	500 lbs. gypsum...................	4007	4554	2336
4	500 lbs. gypsum and lime............	4181	....	....

840 pounds over the check. The plot receiving 200 pounds of gypsum plus lime showed a noticeable increase over the no-lime treatment, but poor yields were obtained on plots 6, 7, and 8, probably due to an attact of gophers in the early spring, and there was no evidence of any effect from the large amounts of gypsum plus lime.

Gypsum had practically no effect on the production of clover hay at the Fort Dodge field and at Eldora only the plot receiving 1000 pounds of gypsum and lime showed an increase in yield of clover hay. A gain of 1410 pounds per

acre of hay was secured on this plot when compared with the plot receiving lime alone and an increase of 750 pounds over the adjacent check.

On the Farson field lime and gypsum produced larger yields of clover hay than lime alone. These increases stand out prominently and amount to almost 1000 pounds of hay per acre. The 200-pound application of gypsum seemed to be more effective than the larger quantities. When gypsum was used without lime it had little effect on the production of clover hay.

The results of the tests with gypsum on clover on the Truesdale, Agency and Stockport fields are given in table 13.

Gypsum, when used either with or without lime, did not have any effect on the yield of clover hay on the Truesdale field. On the Agency and Stockport fields, gypsum was applied as a top dressing on the clover May 13 and 14, 1921, respectively, and the results indicate that the treatments were made apparently too late to permit the gypsum to have any effect.

TABLE 14

The effect of gypsum on alfalfa—Carrington loam

PLOT NUMBER	TREATMENT	YIELD PER ACRE				AVERAGE N IN 2D AND 3D CUTTING
		1st cutting	2d cutting	3d cutting	Total	
		lbs.	lbs.	lbs.	tons	per cent
1	Check..................................	1820	3856	5200	5.43	2.46
2	200 lbs. gypsum........................	2284	4164	5392	5.92	2.45
3	500 lbs. gypsum........................	2108	3868	5568	5.77	2.42

THE EFFECT OF GYPSUM ON ALFALFA

Two 1/40-acre plots were laid out in an alfalfa field on the Agronomy farm of the Iowa Experiment Station in the spring of 1921. They were top-dressed with gypsum on April 14, the first plot at the rate of 200 pounds and the second at the rate of 500 pounds of gypsum per acre.

The results for the three cuttings as well as the average per cent of nitrogen found in the alfalfa from the second and third cuttings are given in table 14.

It will be noted that the gypsum treatments increased the yield of alfalfa hay at each cutting but the effect was most pronounced at the first cutting. The 200-pound application increased the yield of this cutting 464 pounds. At the second cutting the same treatment increased the yield 308 pounds, and at the third cutting an increase of only 192 pounds was secured. The yields from the plot receiving 500 pounds of gypsum per acre were not quite as large as those obtained with the smaller applications.

The total yeild for the three cuttings showed an increase for the 200-pound gypsum treatment of 964 pounds of hay while for the 500-pound application the increase was 668 pounds.

The analyses for total nitrogen on the second and third cuttings show that gypsum did not affect the nitrogen content of the alfalfa hay.

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THE EFFECT OF GYPSUM ON PROTEIN CONTENT OF OATS AND CLOVER

Analyses for total nitrogen were made on samples of oats from the field plots at Ames, Fort Dodge, and Eldora, and also on samples of clover hay from the plots at Ames. The results of these analyses and the per cent of crude protein in each sample are given in table 15.

From the analyses of the clover hay it may be seen that there was a slight decrease in the total nitrogen in the clover on the plots receiving gypsum and lime. This is also true for the 1000-pound gypsum treatment. These differences, however, were too small to be of significance.

TABLE 15

Effect of gypsum on protein content of clover and oats

PLOT NUMBER	TREATMENT PER ACRE	AMES				FORT DODGE		ELDORA	
		Clover		Oats—crude protein		Oats—crude protein		Oats—crude protein	
		Total nitrogen	Crude protein	Grain	Straw	Grain	Straw	Grain	Straw
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
1	Check....................	1.97	12.31	11.03	2.27	10.65	1.92	13.83	4.37
2	200 lbs. gypsum..............	1.98	12.37	Lost	Lost	10.65	1.66	13.30	3.23
3	500 lbs. gypsum..............	1.93	12.06	10.06	1.66	10.65	2.10	12.15	2.88
4	1000 lbs. gypsum.............	1.84	11.50	11.68	1.57	10.65	1.66	11.71	2.88
5	200 lbs. gypsum and lime........	1.70	10.62	10.59	2.36	11.11	2.62	11.89	2.88
6	500 lbs. gypsum and lime........	1.87	11.68	10.40	1.92	11.29	1.92	12.16	2.62
7	1000 lbs. gypsum and lime.......	1.76	11.00	10.15	1.48	11.29	2.62	13.39	2.97
8	Lime.....................	1.89	11.81	10.40	1.66	11.29	....	11.64	2.53
9	Check....................	1.94	12.12	10.59	1.75	11.55	1.83	11.64	2.80

The data presented for the percent of crude protein in the oat grain and straw show that gypsum did not have any marked effect on the total nitrogen content of this crop. The check plots on the Ames and Eldora fields did not agree and hence definite conclusions cannot be drawn.

THE EFFECT OF GYPSUM ON RED CLOVER

Greenhouse Experiment

To check up the data obtained in the field, an experiment was planned to test the effect of gypsum on clover grown in pots in the greenhouse.

The soil obtained for this work was the same as that used in the field test at Ames. It was classed as Carrington loam and had a lime requirement of two tons of $CaCO_3$ per acre. Sixteen 4-gallon stoneware pots were half filled with the subsurface soil, and then the surface soil was added making a total of 35 pounds of soil (air-dry) for each pot. The same treatments used

on the full series of field plots were made in duplicate in this experiment.   The limestone was thoroughly mixed with the surface soils, the pots were weighed and water was added to give optimum moisture conditions.   All the pots were then seeded to red clover.   When the plants were large enough they were thinned to 5 plants per pot and the gypsum treatments were made as a top-dressing and worked into the soil.

The crop was harvested when the majority of the plants were in full bloom and the results obtained from the experiments are given in table 16.

It is rather difficult to draw any definite conclusions from the results.   The 200-pound application of gypsum had no effect on the yield of clover.   The 500-pound treatment on the other hand showed a noticable increase.   The 1000-pound gypsum treatment seems to have had a depressing effect on the yield of the clover.   The pots receiving 200 and 1000 pounds of gypsum with lime showed distinct gains in yields over the pots with lime alone.   The

TABLE 16

The effect of gypsum on yield and nitrogen content of clover in greenhouse experiment

POT NUMBER	TREATMENT	YIELD PER POT—DRY WEIGHT	AVERAGE N CONTENT PER POT
		gms.	*per cent*
1, 2	Check...	19.5	1.69
3, 4	200 lbs. gypsum......	18.5	1.89
5, 6	500 lbs. gypsum...............................	22.0	1.78
7, 8	1000 lbs. gypsum..............................	15.0	2.10
9, 10	200 lbs. gypsum and lime......................	26.0	1.87
11, 12	500 lbs. gypsum and lime.....................	23.0	1.96
13, 14	1000 lbs. gypsum and lime....................	28.5	1.96
15, 16	4 tons lime...................................	24.0	1.83

500-pound gypsum and lime application showed a slight decrease in yield from the lime alone.

Slight increases in total nitrogen content of the clover hay were observed in every case where gypsum was added to the soil but the differences were too small to warrant a definite conclusion.

It is evident from these experiments that yields of oats, barley, rye and clover may be increased on some soils and not on others.   Alfalfa yields were greater when gypsum was used.   The protein content of the various crops, however, was not influenced to any striking extent.

THE EFFECT OF GYPSUM ON SOIL REACTION

At the time the oats crops were harvested from the Ames, Fort Dodge and Eldora fileds, samples of soil were taken from each plot and tested for lime requirement and hydrogen-ion concentration, in order to note the effect of gypsum on soil acidity under actual field conditions.   The samples were taken about 4 months from the time the gypsum applications were made. The results of these tests are shown in table 17.

Examining the pH values for the Ames plots we note that the gypsum treatments had practically no effect on the hydrogen-ion concentration of these soils. The slight increase in acidity (pH 0.11) observed from the 1000-pound application was probably too small to be considered important. The pH values for the Fort Dodge plots also showed that gypsum had no effect whatever on the hydrogen-ion concentration of the soils. A slight increase in acidity (pH 0.2) was noted on the 1000-pound gypsum plot of Eldora field. The 500-pound gypsum application slightly decreased the acidity.

The lime requirement tests checked fairly well in showing that the use of gypsum had little or no effect on the acidity of the soil, as determined by the modified Tacke lime requirement method. From these tests it seems evident

TABLE 17

Effect of gypsum on soil reaction

PLOT NUMBER	TREATMENT (POUNDS PER ACRE)	HYDROGEN-ION CONCENTRATION			LIME REQUIREMENT PER ACRE BY MODIFIED TACKE METHOD		
		Ames	Fort Dodge	Eldora	Ames	Fort Dodge	Eldora
		pH	pH	pH	lbs.	lbs.	lbs.
1	Check............................	6.01	5.39	5.52	4200	7920	4480
2	200 lbs. gypsum....................	6.01	5.35	5.52	4000	8200	5040
3	500 lbs. gypsum....................	5.95	5.37	5.69	4440	6800	4000
4	1000 lbs. gypsum..................	5.90	5.35	5.32	3880	7120	4400
5	200 lbs. gypsum and lime............	6.23	6.01	6.54	3880	4160	2080
6	500 lbs. gypsum and lime............	6.35	7.13	6.17	3520	760	1600
7	1000 lbs. gypsum and lime...........	6.35	5.85	6.37	3060	3360	840
8	Lime.............................	6.37	5.69	6.37	3300	5000	720
9	Check............................	6.44	5.35	5.52	3640	7080	4600

that gypsum in amounts used in ordinary practice did not have any effect on the lime requirement of the soils. When applied at the rate of 200 or 500 pounds per acre it did not raise or lower the hydrogen-ion concentration of the soil as measured by the hydrogen electrode but applications of 1000 pounds caused slight increases in hydrogen-ion concentration on the plots at Ames and Eldora.

THE SULFUR CONTENT OF RAINWATER

During the years 1920–1921 samples of rain and snow were collected on the Agronomy farm of the Iowa Agricultural Experiment Station which is two miles south of Ames. A 4-gallon glazed stoneware crock was used. The samples were stored in bottles sealed with paraffined glass stoppers. The analyses for eighteen months from November 1, 1921 to April 30, 1922 are given in table 18. A total rainfall of 38.17 inches was recorded. The total amount of sulfur added to the soil in the rain and snow for the entire period was 18.34 pounds, or the equivalent of 45.77 pounds of SO_3 per acre.

By comparing the monthly data for sulfur content it may be seen that generally the largest amount of sulfur was brought to the soil during the growing season from March to October when conditions were the most favorable for the bacteria which bring about the decomposition of organic matter with the liberation of hydrogen sulfide. The amount of sulfur found in the rainwater for the spring, summer and fall months was fairly constant, with the exception of July, when only 0.40 pounds of sulfur per acre was obtained. This low figure was probably due to the fact that this month was too dry for vigorous bacterial action.

TABLE 18

Rainfall and sulfur content of rain and snow November 1, 1920, to April 30, 1922

MONTH	RAINFALL		
	Amount	SO₃ content	S content
	in,	*lbs. per acre*	*lbs. per acre*
1920			
November....................	1.08	0.74	0.30
December....................	0.58	0.84	0.34
1921			
January–February............	1.00	5.04	2.02
March.......................	1.28	3.74	1.50
April.......................	2.91	5.49	2.20
May........................	2.83	4.57	1.83
June........................	4.77	2.67	1.07
July........................	1.11	1.00	0.40
August......................	7.35	5.47	2.19
September...................	6.76	3.77	1.51
October.....................	1.25	3.67	1.47
November–December...........	1.12	1.75	0.70
1922			
January–February............	1.93	2.32	0.93
March.......................	1.50	1.53	0.61
April......................	2.70	3.17	1.27
Total.....................	38.17	45.77	18.34

Other investigators have shown that the amount of sulfur added to the soil in the rainwater does not vary greatly from year to year. A total of 14.89 pounds of sulfur was added to an acre of soil during the year 1921 and the annual precipitation was about average. It may be concluded therefore that from twelve to sixteen pounds of sulfur per acre may be regarded as the average amount of sulfur which is added to the soil by the rainwater under actual farm conditions in Iowa.

THE AMOUNT OF SULFUR IN DRAINAGE WATER

A study of the loss of sulfur in drainage water was made during the year 1921–22. A 4-gallon glazed stoneware pot was placed on a small platform. The small drainage opening near the bottom of the pot was fitted with a small metal spigot, the outlet of which entered a smaller glazed stoneware pot through an improvised galvanized cover. The cover was arranged to exclude particles of dust as well as rainwater.

A layer one inch thick of carefully washed sulfur-free sand was placed in the bottom of the upper pot. Fresh Carrington loam surface soil was then added making a total depth of six inches of soil which included a good clover sod.

TABLE 19

Loss of sulfur in drainage water

MONTH	DRAINAGE WATER	WEIGHT BaSO$_4$ PER 250 CC. DRAINAGE WATER	RELATION OF S LOST TO TOTAL DRAINAGE WATER
1921	*cc.*	*gm.*	*per cent*
April	225	0.0389	0.00213
August	1378	0.0377	0.00206
September	5870	0.0315	0.00172
1922			
February	265	0.0404	0.00221
March	1000	0.0322	0.00176
April	2450	0.0414	0.00226
Average			*0.00202*

During the year 1921, the rainfall was so scattered over each month that drainage water from the soil in the pot was collected only during the months of April, August, and September. In 1922 drainage water was obtained during the months of February, March, and April. The results secured for these analyses are given in table 19.

Although the amount of drainage water obtained during the months noted in the table varied greatly, there was a striking uniformity in the analyses for total sulfur lost and the per cent lost was almost constant.

Sulfur averaged .00202 per cent of the drainage water from this soil. One inch of rain per acre weighs 226,000 pounds. From a study of a number of investigations it seems that 50 per cent of the total rainfall is lost in the drainage water. Using these figures, the calculated loss of sulfur from a 30-inch rainfall on the Carrington loam would be 67.5 pounds per acre per year.

The amount of sulfur lost in the drainage was over four times as great as that added to the soil by the rain and snow. While this applies only to the Carrington loam, the sulfur lost from other types of soil is probably quite as

great.   It is quite apparent that the continued loss of sulfur at this rate will lead to a rapid depletion of the native sulfur supply of the soil.

GENERAL CONCLUSIONS

Some important conclusions may be drawn from this work.   In the first place it is quite apparent from both the chemical data and field work that the soil type plays a prominent part in the effects of gypsum on soils.   With certain soils gypsum in the amounts usually employed in agricultural practice affected the soil phosphorus and the soil potassium, rendering both of these constitutents more soluble in a water-extract.   With other soils little or no effect was observed.   When gypsum was used in excessive quantities, however, there was a marked increase in the amount of water-soluble potassium in all the soils studied.

The smaller applications of gypsum did not have any effect on ammonification and nitrification, while the larger amounts were slightly unfavorable to these bacterial processes.   All of the gypsum treatments were unfavorable to azofication as measured by the amount of nitrogen fixed in solution per gram of dextrose.

The results on carbon dioxide production show that gypsum did not hasten the decomposition of the soil organic matter except perhaps, in a highly basic soil.

In the field experiments, gypsum proved favorable on the clover and small grain crops in several instances.   Possibly the effects on clover would have been more pronounced had the applications been made as top-dressings directly to the clover instead of to the grain crops.

Gypsum at the rate of 200 pounds per acre exerted a distinctly beneficial effect on the production of alfalfa hay.   It was unfortunate that the results of the experiments on alfalfa were limited to one field, because it is believed that greater increases from the use of gypsum would be noted on alfalfa than on other crops.

Finally the analyses of rain and drainage waters emphasize further the importance of the sulfur problem in agriculture.   The amount of sulfur lost in the drainage is far greater than that added to the soil in the rainwater.   It is quite evident that even though soils may be well supplied with sulfur at the present time this sulfur is constantly being oxidized to the sulfate in which form it is readily leached away in the drainage waters.   If any system of soil fertility is to be permanent, a provision must be made for the addition of sulfur in some form to the soil.   This may be accomplished economically through the use of barnyard manure, gypsum or acid phosphate which contains about 60 per cent of gypsum.